Faculty Publications

1994-09-01

The structure and dynamics of the CS₂ molecular ion

Karl Sohlberg

Chan Yibai

Follow this and additional works at: <https://scholarsarchive.byu.edu/facpub>

Part of the [Biochemistry Commons](#), and the [Chemistry Commons](#)

Original Publication Citation

Sohlberg, Karl and Yibai Chen. "The structure and dynamics of the CS₂ molecular ion." The Journal of Chemical Physics 11 (1994): 3831-3839.

BYU ScholarsArchive Citation

Sohlberg, Karl and Yibai, Chan, "The structure and dynamics of the CS₂ molecular ion" (1994). *Faculty Publications*. 697.

<https://scholarsarchive.byu.edu/facpub/697>

This Peer-Reviewed Article is brought to you for free and open access by BYU ScholarsArchive. It has been accepted for inclusion in Faculty Publications by an authorized administrator of BYU ScholarsArchive. For more information, please contact ellen_amatangelo@byu.edu.

The structure and dynamics of the CS_2^+ molecular ion

Karl Sohlberg and Yibai Chen

Department of Chemistry, Brigham Young University, Provo, Utah 84602

(Received 19 August 1993; accepted 24 May 1994)

Several common elementary methods of computing molecular properties, prerequisite to molecular dynamics studies, are tested for their validity for CS_2^+ . Judged sufficiently accurate, these methods are then used to aid in investigating the collisionally activated dissociation of CS_2^+ upon impact with xenon. Rice–Ramsperger–Kassel–Marcus (RRKM) unimolecular decay rate calculations are presented and compared to experimental studies employing collisional activation. RRKM theory is shown to reproduce the experimental results for collision energies near threshold. When corrected for vibrational anharmonicity, the RRKM calculation shows agreement with the experimental results over a slightly wider range of energies. A discussion is given on the applicability of the “adiabatic criteria” to describing electronic excitations in the collisional activation process. This model is shown to provide a better description of the activation process than direct vertical excitation.

I. INTRODUCTION

The fragmentation of collisionally activated ions is often studied by tandem mass spectrometry.¹ Indeed, collisionally activated dissociation (CAD)² has reached the state of being an analytical tool in the field of mass spectrometry.³ The dissociation is widely accepted to follow the historic Lindemann⁴ mechanism, whereby the ion is excited in a bimolecular collision leading to an energetically activated species which subsequently undergoes internal energy redistribution followed by dissociation. The activation process is thought to be vibrational excitation in low energy collisions and by excitation to an excited electronic state in higher energy collisions.⁵ The low energy process is accepted to be describable with the Rice–Ramsperger–Kassel–Marcus (RRKM) unimolecular dissociation rate theory.⁶ The electronic excitation process is often postulated to be described by the “adiabatic criteria.”^{7,8}

The above models give a simple intuitive picture of the CAD mechanism and are often discussed in a qualitative way when results of CAD experiments are presented. Unfortunately, it is rare that these models are actually applied in any concrete manner to specific CAD systems. Recently, however, Prinslow and Armentrout⁹ have reported the results of detailed CAD experiments on a system of sufficient simplicity that these long accepted models can be applied. Earlier CAD studies of the CS_2^+ ion were reported by Hirst *et al.*⁵ The CAD of CS_2^+ in kilovolt energy collisions has also been studied.^{10–12}

In order to undertake molecular dynamics calculations, it is first necessary to obtain certain molecular parameters. Of paramount importance are the molecular vibrational frequencies. This is true whether a simple model such as RRKM is used, or a more sophisticated one. When experimental values for the molecular vibrational frequencies are not available, they are often obtained with Hartree–Fock self-consistent field (HF-SCF) methods. Several papers by Person and co-workers contain relevant examples.^{13–15} More recent work on the CS_2^+ ion has been presented by Brommer and Rosmus.¹⁶ Semiempirical methods afford an enormous savings in computational time over *ab initio* methods and there-

fore their accuracy in predicting molecular vibrational frequencies has also been investigated.¹⁷ When standard software is used, however, the frequencies produced by HF-SCF calculations may not have the proper symmetry properties. A procedure for computing properly symmetry adapted frequencies is given here. The resulting frequencies show good agreement with experimental results.

Franck–Condon factors (FCFs) are essential for studying direct electronic excitation processes (see Herzberg for a thorough discussion.¹⁸ Simple analytic expressions, derived by Sharp and Rosenstock, give FCFs of reasonable accuracy.¹⁹ In this paper, FCFs obtained with this method are used to aid in understanding the CAD dynamics of the $\text{CS}_2^+ + \text{Xe}$ system. The results indicate that mechanisms involving vertical (Franck–Condon type) excitations of the CS_2^+ ion do not play a major role in the low energy CAD of CS_2^+ .

Herein, the RRKM model of unimolecular dissociation is applied to the $\text{CS}_2^+ + \text{Xe}$ system. The results support the long held belief that low energy CAD involves vibrational excitation followed by internal energy redistribution and subsequent dissociation, but only over a limited energy range. The applicability of the adiabatic criteria is also considered and found to give some insight into the CAD mechanism when a “modern” perspective is taken of the interacting electronic states.²⁰

The purpose of this paper then is twofold. First, several commonly used methods of obtaining information about molecular structure and dynamics are tested on the CS_2^+ system to confirm their applicability. Second, having established the validity of these methods for CS_2^+ , they are employed to further understand the CAD of the $\text{CS}_2^+ + \text{Xe}$ system.

II. ELECTRONIC STRUCTURE

Structural information for CS_2^+ has been obtained previously with computational methods^{15,21} and emission spectroscopy.^{22,23} The electronic states of CS_2^+ have been investigated extensively by photoelectron spectroscopy.^{24–28} Multiphoton absorption spectroscopy^{29,30} has also been used to elucidate the nature of the *C* state of CS_2^+ . Mathur and

TABLE I. A comparison of the computed equilibrium structure of CS_2 with that determined from experimental work. R_e is the separation of the carbon atom from either S atom and is given in Ångströms. Computed and experimental force constants for CS_2 are also given in units of mdyn/Å.

Method	Geometry	R_e
RHF	$D_{\infty h}$	1.571
Expt. ^a	$D_{\infty h}$	1.554
Method	$k(\text{stretch})$	$k(\text{bend})$
RHF	7.6	0.21
Expt. ^b	7.5	0.23

^aReference 35.

^bReference 40.

Harris have reviewed the application of mass spectral methods to the positively charged ions of CS_2 .³¹ Tabulations of appearance potentials, ionization potentials, heats of formation, and other energetic data for CS_2^+ can be found in Franklin *et al.*³² and Rosenstock *et al.*³³ Vibrational frequencies have been tabulated by Jacox.³⁴ In order to further understand the electronic structure of CS_2 and CS_2^+ , and to complement these literature results, some calculations have been performed here.

As a first step, the symmetries of the valence molecular orbitals of CS_2 were determined. The geometry of CS_2 was assumed to be $D_{\infty h}$ as reported by Herzberg.³⁵ A basis set of 12 atomic functions was employed ($2s$, $2p_x$, $2p_y$, $2p_z$ on carbon and $3s$, $3p_x$, $3p_y$, $3p_z$ on each sulfur). This basis set was transformed under the $D_{\infty h}$ symmetry operations and the resulting representation was reduced to find the symmetries of the molecular orbitals. Twelve molecular orbitals result—three of symmetry Σ_g^+ , three of symmetry Σ_u^+ , one of symmetry Π_g , and two of symmetry Π_u .

Next an extended Hückel (EHT) semiempirical calculation of the molecular orbitals of CS_2 was performed. The same basis set was used as in the group theory analysis. Details of the EHT calculation are given in the Appendix. The resulting molecular orbitals have the expected symmetries. The highest occupied molecular orbital (HOMO) is a degenerate pair of Π_g symmetry. The EHT calculation predicts that these orbitals are nonbonding combinations of only the sulfur $3p_x$ and $3p_y$ atomic orbitals, in agreement with Mathur *et al.*³¹ These orbitals lie at an energy of -0.42 hartree and predict, by Koopmans' theorem,³⁶ an ionization energy of CS_2 of about 11.4 eV, leading to a $^2\Pi$ ground state of CS_2^+ . This is somewhat above the experimentally accepted value of 10.1 eV.^{31,37,38}

While the group theoretical analysis and EHT calculation give some insight into the electronic structure of CS_2 in order to gain a more complete understanding, it is useful to invoke a higher level theoretical treatment. A HF-SCF calculation was performed for CS_2 . The largest readily available triple-zeta Gaussian basis set was used (6-311G). This basis gives SCF limit energies to $1/10\,000$ in atomic calculations of carbon and sulfur.³⁹ First, the geometry was optimized and found to agree with the well-known $D_{\infty h}$ structure. Table I gives a comparison of the results.

The local mode bond-stretching force constant for CS_2 was computed by evaluating the energy at three geometries

TABLE II. RHF energy levels of CS_2 . Column " d " gives the degeneracy, column "pln" gives the number of nodes parallel to the principle axis, column "ppn" gives the number of perpendicular nodes, and "energy" is the orbital energy in electron volts.

State	d	pln	ppn	Energy	Notes
LUMO	2	1	2	1.19	
HOMO	2	1	1	-10.2	Ionizes to $X\ ^2\Pi\ \text{CS}_2^+$
2HOMO	2	1	0	-14.6	Ionizes to $A\ ^2\Pi\ \text{CS}_2^+$
3HOMO	1	0	3	-15.8	Ionizes to $B\ ^2\Sigma\ \text{CS}_2^+$
4HOMO	1	0	2	-18.4	Ionizes to $C\ ^2\Sigma\ \text{CS}_2^+$

along the stretching mode and fitting them to a quadratic function. The bending force constant was found in a similar fashion. The RHF values are in good agreement with those of Wilson, Decius, and Cross,⁴⁰ which were obtained from experimentally known vibrational frequencies. For the results, see Table I.

As in the EHT calculation, the HOMO was found to be composed exclusively of nonbonding sulfur atomic $3p_x$ and $3p_y$ orbitals. As pointed out by Mathur,³¹ this suggests that the structure of CS_2 should be relatively insensitive to the removal of one or two electrons from the HOMO, which is observed experimentally.^{22,35} This insensitivity of the structure to ionization has important implications in interpreting photoionization results as will be elaborated upon in Sec. V A. Table II shows the states near valence of CS_2 as computed with HF-SCF theory. Note that Koopmans' theorem ionization energy of 10.2 eV is in excellent agreement with the experimental value of 10.1 eV.^{31,37,38}

By using Koopmans' theorem on the HF-SCF results, the four lowest states of the CS_2^+ molecular ion can be approximated. A comparison with experimental results is shown in Table III. Note that even large basis set SCF calculations such as these give excited state energies whose accuracy is fair at best.

III. FREQUENCY ANALYSIS

Next, harmonic analysis was performed on the optimized geometry of CS_2 . The results are compared with experimental values in Table IV. The agreement is very good. This is not unexpected because the HF-SCF calculation produced very accurate force constants. To undertake a RRKM^{6,41} calculation of unimolecular dissociation rates, the reactant and product vibrational frequencies are needed. If these frequencies have not been established experimentally, it is customary to compute them with *ab initio* methods. The HF-SCF method is often employed because numerous user-friendly

TABLE III. States of CS_2^+ . $E(\text{exp})$ are experimental values (Ref. 38). Energies are in electron volts. The ground state of the molecule is taken as the zero of energy for purposes of comparison to PES data.

State	$E(\text{exp})$	$E(\text{HF})$
$X\ ^2\Pi_g$	10.08	10.2
$A\ ^2\Pi_u$	12.63	14.6
$B\ ^2\Sigma_u^+$	14.47	15.8
$C\ ^2\Sigma_g^+$	16.19	18.4

TABLE IV. Vibrational frequencies of CS₂. All values are in cm⁻¹.

Method	ω_1	ω_2	ω_3
RHF-SCF	661	376,376 ^a	1530
Expt. ^b	657.98	396.7	1532.5

^aDegenerate.^bReference 35.

software packages are available for performing such calculations. In the case of CS₂⁺, e.g., it is not unreasonable to expect that SCF theory will produce accurate values for the normal mode frequencies since the computed frequencies for CS₂ are in good agreement with experimental results. These were computed and are given in Table V. It should be noted that the computation of these frequencies was not as straightforward as computing those for CS₂. To accommodate the ionic character of CS₂⁺, polarization and diffuse functions were added to the basis set yielding (6-311+G*). Both the Gaussian⁴² and GAMESS³⁹ programs predict four unique frequencies for CS₂⁺ when directed to find the vibrational frequencies. This is not reasonable given the *D_{∞h}* equilibrium geometry. Initially, it was suspected that the equilibrium geometry might deviate slightly from *D_{∞h}*, but careful optimization of the structure showed this to be false. Any deviations from linearity were determined to be less than 10⁻⁵ Å in the HF-SCF approximation. A third *ab initio* program, Spartan,⁴³ was used to compute the frequencies and it produced the expected degenerate Π bending mode and two unique Σ modes.⁴⁴ To confirm the Spartan result, the frequencies were computed by directly diagonalizing the mass-weighted Cartesian force constant matrix.^{41,45} The Cartesian force constants were approximated by taking numerical second derivatives of the potential as follows:

$$\frac{\partial^2 V}{\partial x^2} \approx [V(x+\Delta x) - 2V(x) + V(x-\Delta x)]/(\Delta x)^2, \quad (1)$$

$$\begin{aligned} \frac{\partial^2 V}{\partial x \partial y} \approx & [V(x+\Delta x, y+\Delta y) - V(x+\Delta x, y-\Delta y)]/(4\Delta x \Delta y) \\ & + [-V(x-\Delta x, y+\Delta y) \\ & + V(x-\Delta x, y-\Delta y)]/(4\Delta x \Delta y), \end{aligned} \quad (2)$$

where *x* and *y* are arbitrary Cartesian nuclear coordinates. The step size for the numerical differentiation was taken as Δ*x*=Δ*y*=0.01 Å. This procedure requires sampling the potential at four geometries to find each off-diagonal element of the force constant matrix and at two geometries to find each diagonal element. The potential at the equilibrium ge-

TABLE V. Vibrational frequencies of CS₂⁺. All values are in cm⁻¹.

Method	ω_1	ω_2	ω_3
Spartan ^c	663	306,306 ^a	1152
Direct	664	304,304 ^a	1156
Expt.	676 ^b	306 ^b	1161 ^b

^aDegenerate.^bFrom Ref. 26.^cReference 43.

ometry must also be calculated for a total of 307 geometries. The force constant matrix is symmetric about the diagonal, however, reducing the number of required single point calculations to 163. The computed vibrational frequencies are in excellent agreement with those produced by the Spartan program. Agreement is also good with experimentally determined values. These single point calculations were done with Gaussian 90, using the full polarized and augmented triple zeta basis set 6-311+G*. The use of molecular symmetry in computing the integrals was disabled in these single point calculations.⁴⁶

Note also that in ionizing from CS₂ to CS₂⁺, the vibrational frequencies drop slightly, which is to be expected because the bonding is slightly weaker in CS₂⁺. This change is small, however, because the valence electrons come from nonbonding atomic 3*p_x* and 3*p_y* orbitals.

The results of this section indicate that while standard HF-SCF methods can produce reasonably reliable molecular vibrational frequencies, it is necessary to check that the computed frequencies have degeneracies in accordance with the molecular symmetry. If the vibrational frequencies are not properly symmetry adapted, correct results can be obtained by diagonalizing the full Cartesian force constant matrix constructed by computing numerical derivatives of the molecular potential from single point calculations.

IV. RRKM UNIMOLECULAR DISSOCIATION RATES

The success of RRKM theory in describing unimolecular dissociation reactions is so widespread, that it has been claimed that "No well-documented ionic reaction which occurs on the ground-state potential energy surface has been shown to have a rate constant in disagreement with that of RRKM theory".⁴¹ This bold statement suggests that RRKM theory is a good place to start when looking for a theoretical explanation of the dissociation of collisionally activated CS₂⁺ ions, although the presence of multiple electronic states may impair its success.

The RRKM unimolecular decay rate constant is given by^{6,41}

$$k(E) = \left(\frac{1}{h} \right) \left[\frac{G(E^\ddagger)}{N(E)} \right], \quad (3)$$

where *G*(*E*[‡]) is the sum of states accessible to the transition state with internal energy *E*[‡]=*E*−*E*₀, *E* being the total energy available and *E*₀ being the energy required to reach the transition state from the activated molecule (potential energy difference). *N*(*E*) is the density of states of the activated molecule, CS₂⁺* in this case, at an energy *E*, and *h* is Planck's constant. Since the rotational energy is small in comparison with the internal vibrational energy, the external rotational energy is neglected in this calculation. The transition state can be taken to be at some positive distance along the reaction coordinate. The activated complex is at the equilibrium separation, but has some large value for the internal energy in excess of the dissociation energy *D*₀. Products are of course at *R*=∞. Figure 1 shows the relationship of the activated complex, transition state, and products. The unimolecular dissociation of CS₂⁺ is assumed to be a simple bond

FIG. 1. A relationship of the activated complex $(\text{CS}_2^+)^*$, transition state $(\text{CS}\cdots\text{S}^+)^*$, and products with associated energies.

cleavage process and the recombination has no activation barrier. While the formation of ground state products S^+ ($^4\text{S}_u$) and CS ($^1\Sigma^+$) from the $X^2\Pi_g$ ground state of CS_2^+ is spin forbidden,^{47,48} the simple bond cleavage pathway is justified by a body of experimental work which has shown the production of S ions at the thermodynamic threshold indicating strong spin-orbit coupling.^{9,25}

Now one must ask "What is the density of states of the activated complex at energy E ?" Since E is necessarily above the threshold for dissociation, there are no true bound states. The complex is in the continuum and therefore the density should be infinite. The same problem exists for the sum of states of the transition state at energy $E^\ddagger = E - D_0$. If $E^\ddagger$ is greater than the strength of the weakest bond in the transition state, it is in the continuum and the sum of states will be infinite. This makes $k(E) = \infty/\infty$, which is undefined. What is one to do in this situation? A more fundamental way of expressing the above question is "What does the density of states function $N(E)$ look like for energies $E > D_0$?"

The first thing to note is that the usual expressions for G and N assume harmonic oscillator potentials for all bonds except the one which is breaking and thus there is no continuum and hence no problem with infinite state density.⁴⁹ Since most real vibrations will become anharmonic at sufficiently high values of their internal energy, the harmonic approximation will necessarily break down with increasing energy. In fact, Forst notes that the anharmonicity, and subsequent dissociation, of real molecular vibrational modes is the major limitation on accuracy in determining the values of $N(E)$ and $G(E)$.⁶ The next thing to note is that for a polyatomic molecule, there will be many quasibound states (resonances) above the dissociation limit which represent holding small amounts of energy in each bond, the sum of which is in excess of the dissociation energy. One can count these resonances in determining $G(E)$ and $N(E)$. The same holds true for a polyatomic transition state. The states above D_0 given by the harmonic approximation are approximations to these "resonances" in the physical system. Since these resonances are real physical entities which the system can sample, it is

appropriate to enumerate them when determining the values of $G(E)$ and $N(E)$.

One might argue that to obtain the best accuracy, the vibrational states should be computed *ab initio*. This would avoid any limitations of approximate enumeration schemes. Unfortunately, such an approach is not currently feasible. Using the harmonic approximation, one finds that there are more than 10^6 bound vibrational states of CS_2^+ . While using a rather crude approximation, this result shows that computing all of the vibrational states of CS_2 by standard variational methods is out of the question. This is true in spite of the great advances made in this area.⁵⁰ It is simply true that even with a minimal basis set, one would need to diagonalize a matrix of about 10^{12} elements. Furthermore, the resulting table of eigenvalues, which would correspond to the vibrational energy levels, would be so large as to be nearly useless. On the positive side, the existence of so many vibrational levels suggests that a RRKM calculation may not be unreasonable even for this triatomic system.

To proceed with the RRKM calculation, first the vibrational frequencies of the activated complex and the transition state must be known. The vibrational frequencies of CS_2^+ are already available. The vibrational frequencies of the transition state were determined as follows: When CS_2^+ decomposes into CS^+ and S (or CS and S^+), the degenerate bending mode of CS_2^+ decays into a degenerate rotational mode of the CS^+ (or CS) fragment.⁵¹ Since rotational periods are generally longer than vibrational periods, the rotational frequency of the CS^+ (or CS) fragment is expected to be lower than the frequency of the bending mode of vibration of CS_2^+ . If the CS fragment is assumed to be a rigid rotor of reduced mass μ and separation r_e , by substituting the quantum expression for the energy of a rigid rotor into the classical expression for the rotational frequency,⁵² the rotational frequency is found to be

$$w = 2.32 \text{ cm}^{-1}. \quad (4)$$

The Π mode of vibration of the transition state was assumed to have a frequency between that of the Π bending mode of vibration of CS_2^+ and the degenerate rotational mode of the CS^+ (or CS) fragment⁵³

$$\omega^\ddagger = \frac{303.87 + 2.32}{2} = 153 \text{ cm}^{-1}. \quad (5)$$

The stretching mode of vibration of the transition state was assumed to be equal to that of CS in the case of $\text{CS} + \text{S}^+$ as products, and that of CS^+ in the case of $\text{CS}^+ + \text{S}$ products. This procedure of approximating the transition state frequencies follows the recommendations of Forst.⁶ The vibrational frequencies are collected in Table VI. Other relevant values are collected in Table VII.

The unimolecular dissociation rate was computed as a function of energy for both the $\text{CS}_2^+ \rightarrow \text{CS}^+ + \text{S}$ channel $k_1(E)$, and the $\text{CS}_2^+ \rightarrow \text{CS} + \text{S}^+$ channel $k_2(E)$. While a unimolecular dissociation rate constant for the activated species CS_2^{+*} is not related to the phenomenological cross section which defines an effective bimolecular rate constant for the overall reaction, the ratio of the rate constants for the two competing channels will be equal to the ratio of the cross

TABLE VI. Vibrational frequencies used in the RRKM calculation. All reported places were used. The uncertainties are given in the original sources. All values are in cm^{-1} .

System	ω_1	ω_2	ω_3	ω_4
CS_2^{+*}	1155.93 ^b	663.93 ^b	303.87 ^b	303.87 ^b
CS_2^{+d}	1285.08 ^a	153 ^c	153 ^c	...
CS_2^{+e}	1384 ^a	153 ^c	153 ^c	...
CS	1285.08 ^a	...	...	...
CS^+	1384 ^a	...	...	...

^aFrom Ref. 68.

^bFrom HF-SCF calculations.

^cInterpolated.

^dCS product.

^e CS^+ product.

sections. The ratio $k_1(E)/k_2(E)$ is shown in Fig. 2 (solid curve). This is compared with the ratio $\sigma_1(E)/\sigma_2(E)$, the ratio of the experimental cross sections for the two reactions as measured by Prinslow and Armentrout.⁹ As seen in Fig. 2, the RRKM value falls within the experimental error from threshold up to 7.3 eV (with one minor excursion near 6.9 eV).

In order to improve the RRKM calculation, an attempt was made to account for the anharmonicity of the vibration. For the highest frequency stretching mode of both the activated complex and the transition state, the vibrational states were assumed to be given by the expression

$$E_n = (n + 0.5)\omega_e - (n + 0.5)^2\omega_e x_e. \quad (6)$$

This expression is in the form of the exact levels of a Morse type oscillator. Unfortunately, the normal frequency calculation using HF-SCF theory gives only the value of ω_e . To obtain the anharmonicity constant $\omega_e x_e$, a method was used which was given by Morse in his paper describing the exact solution of the quantum energy levels of what has come to be called a "Morse" potential.⁵⁴ Morse gives

$$D_e = \frac{\omega_e^2}{4\omega_e x_e}, \quad (7)$$

from which the anharmonicity constants for the symmetric stretching modes of the activated complex and the transition state were approximated. The other modes were allowed to

TABLE VII. Miscellaneous values used in the RRKM calculations.

System	Notes
CS	$D_0 = 7.35 \text{ eV}^a$
CS	$D_e = 59\,925 \text{ cm}^{-1a}$
CS	$\omega_e = 1285.08 \text{ cm}^{-1a}$
CS	$\omega_e x_e = 6.46 \text{ cm}^{-1a}$
CS^+	$D_0 = 6.38 \text{ eV}^a$
CS^+	$D_e = 52\,150 \text{ cm}^{-1a}$
CS^+	$\omega_e = 1384 \text{ cm}^{-1a}$
CS_2^{+c}	$D_0 = 37\,101 \text{ cm}^{-1b}$
CS_2^{+d}	$D_0 = 45\,973 \text{ cm}^{-1b}$

^aFrom Ref. 68.

^bFrom Ref. 35.

^cCS product.

^d CS^+ product.

FIG. 2. A comparison of the RRKM results to the experimental results of Prinslow and Armentrout (Ref. 9) for the CAD reaction $\text{CS}_2^+ + \text{Xe} \rightarrow \text{products}$. (Points with error bars) expt; (solid curve) RRKM using harmonic sum of states; (dashed curve) RRKM with anharmonicity correction.

remain harmonic. When the $G(E)$ and $N(E)$ values are computed with this anharmonicity correction, the ratio of the rate constants is given by the broken curve in Fig. 2. The RRKM result now agrees with the experimental values up to 7.8 eV collision energy. As might be anticipated, when the anharmonicity of the vibration is accounted for, RRKM theory holds for somewhat higher energies. Above 7.8 eV collision energy, RRKM theory fails to predict the experimental results, however, and other models must be sought to describe the experimental results.

It is desirable to establish the sensitivity of the computed product ratio to the estimated vibrational frequencies. Since the Π mode of vibration of the transition state is the lowest frequency vibration used in the calculation, and the least accurately known, the stability of the computed product ratio was established with respect to changes in this frequency. The frequency of this mode was changed by 50% and the product ratio recomputed. For energies between 5.8 and 9.0 eV, the average change in the product ratio was 4.6% and the maximum change was only 14.9%. Above 9.0 eV, the RRKM calculation is much less stable, with changes in the product ratio of more than 60%. Above 9.0 eV, however, the RRKM calculation is not valid and any instability is of no consequence. The other vibrational frequencies used in the RRKM calculation are much more accurately known. In addition, the computed product ratio is less sensitive to changes in the larger frequencies. The conclusion is that within the uncertainty of the frequencies used, the computed product ratio is quite stable.

V. THE MECHANISM OF EXCITATION

A. The role of vertical transitions

In order to ascertain the importance of direct vertical electronic excitations in a CAD reaction, it is essential to have available Franck-Condon factors for those electronic transitions. If experimentally determined values are not available, as is commonly the case for transitions originating

TABLE VIII. A comparison of experimental Franck–Condon factors with those computed with the method of Sharp and Rosenstock (Ref. 19). The results (when numerical) are normalized so that the sum of all vibrational contributions to a given electronic transition is 1.0. The $\text{CS}_2^+ \leftarrow \text{CS}_2$ results are from Brundle and Turner (Ref. 24). The $\text{CS}_2^+ \leftarrow \text{CS}_2^+$ results are from Balfour (Ref. 23).

Transition	Vibrational component	Experimental factor	Calculated factor
$X \text{ CS}_2^+ \leftarrow X \text{ CS}_2$	000	1.0	0.974
$X \text{ CS}_2^+ \leftarrow X \text{ CS}_2$	020	≈ 0.05	0.016
$X \text{ CS}_2^+ \leftarrow X \text{ CS}_2$	040	≈ 0.025	...
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2$	000	0.105	0.130
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2$	100	0.216	0.275
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2$	200	0.252	0.281
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2$	300	0.189	0.184
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2$	400	0.124	0.087
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2$	500	0.070	0.031
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2$	600	0.031	0.009
$B \text{ CS}_2^+ \leftarrow X \text{ CS}_2$	000	0.89	0.945
$B \text{ CS}_2^+ \leftarrow X \text{ CS}_2$	100	0.10	0.050
$B \text{ CS}_2^+ \leftarrow X \text{ CS}_2$	200	0.01	...
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2^+$	000	$>0.136, <0.203$	0.131
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2^+$	100	$>0.219, <0.377$	0.280
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2^+$	200	$>0.298, <0.344$	0.285
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2^+$	300	$>0.188, <0.234$	0.183
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2^+$	400	...	0.083
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2^+$	500	...	0.029
$A \text{ CS}_2^+ \leftarrow X \text{ CS}_2^+$	600	...	0.007
$B \text{ CS}_2^+ \leftarrow X \text{ CS}_2^+$	000	vvs	0.940
$B \text{ CS}_2^+ \leftarrow X \text{ CS}_2^+$	100	mw	0.052

from the ground (X) state of a molecular ion, it is necessary to resort to computational techniques. In general, the computation of Franck–Condon factors for other-than-diatomic molecules is a complex task requiring extensive knowledge of both the initial and final state wave functions. Sharp and Rosenstock,¹⁹ however, have given general expressions for calculating Franck–Condon factors for linear triatomic molecules based on the harmonic approximation which give results in reasonable agreement with experimentally determined values. A comparison of experimentally determined values to those obtained with the method of Sharp and Rosenstock is given in Table VIII. Brundle and Turner have made a similar comparison for transitions from CO_2 to CO_2^+ .²⁴

Two important conclusions can be drawn from the data in Table VIII. First, the relative intensities of electronic transitions in triatomic molecules can be predicted with reasonable accuracy using the method of Sharp and Rosenstock. Second, the intensities of transitions to the various vibrational levels of the A and B electronic states of CS_2^+ from the X state of CS_2^+ are very similar to the intensities of transitions to those same levels from the X state of CS_2 . The remarkable similarity of the Franck–Condon factors for transitions arising from these two initial states is a consequence of the similarity of the structure of the CS_2 ground state potential energy surface to that of the ground state of CS_2^+ (see Sec. II). The equilibrium bond lengths of the ground states of CS_2 and CS_2^+ differ by only 0.0003 Å (Ref. 22) and the vibrational frequencies differ by less than 15%.³⁴ Since variations in equilibrium bond length have a far greater ef-

FIG. 3. A comparison of the product ratio $(\text{CS}^+)/(\text{S}^+)$ observed by Prinslow and Armentrout (Ref. 9) (solid points), and Hirst *et al.* (Ref. 5) (open circles) to that observed from photodissociation of CS_2 by Coppens *et al.* (Ref. 25), (solid curve). The photodissociation curve is shifted by the ionization potential of CS_2 for purposes of comparison. The positions of the C and D states are marked.

fect on the FCFs than changes in the vibrational frequencies,⁵⁵ the similarity of the transition intensities is to be expected.

If the CAD of CS_2^+ was to take place by a mechanism whereby the reactant ion CS_2^+ was excited in the collision by a vertical excitation and subsequently underwent unimolecular fragmentation, one would expect the product ratio $(\text{CS}^+)/(\text{S}^+)$ to be virtually identical to that seen in photodissociation experiments of the CS_2^+ ion since the excitation in these experiments is almost certainly by vertical transition. Unfortunately, the data on photofragmentation of CS_2^+ are either at energies below the threshold for production of CS^+ ,⁵⁶ or involve an initial state other than the X state of CS_2^+ .⁵⁷ In light of the similarity in the FCFs for transitions arising from the ground state of CS_2 to those arising from the ground state of CS_2^+ , as discussed in the last paragraph, it is expected that the product ratio $(\text{CS}^+)/(\text{S}^+)$ resulting from photofragmentation of CS_2 will be an excellent predictor of the ratio which would be produced from photofragmentation of CS_2^+ . This ratio has been computed from the results of Coppens *et al.* and is shown in Fig. 3.²⁵ The energy, of course, is shifted by the ionization potential of CS_2 . Note that there are no interferences from Rydberg states of the CS_2 molecule in the energy range of interest (for several electron volts above the threshold for production of CS^+).²⁵ It can be seen that there is a large increase in the production of the CS^+ fragment ion when the C state of CS_2^+ becomes energetically accessible. This is a consequence of predissociation from the C state.^{47,48} The CS^+ fragment is dominant in the breakdown of $C \text{ CS}_2^+$.^{30,31} A similar increase in the dominance of the CS^+ ion is seen when the D state becomes energetically accessible. The D state is also predissociated.⁴⁸ Gebelein and Jortner,⁵⁸ who extended the work of Gilbert and Ross,⁵⁹ have shown that abrupt fluctuations such as these are to be expected in the case of predissociation. Figure 3 shows that there is essentially no agreement between the product ratio predicted by the photodissociation mechanism

and that observed in the CAD studies. Most notably, there is no abrupt increase in the CS^+ product with respect to the S^+ product when the C and D states of CS_2^+ are reached in the CAD results. It is unlikely, therefore, that direct vertical electronic excitations play any significant role as an excitation mechanism in the CAD of CS_2^+ .

Timing arguments further support the contention that reactant excitation in the low energy CAD of CS_2^+ does not occur by direct vertical electronic excitation. The collision time (defined to be the duration of time it takes the projectile to pass through the region in which the target and the projectile are interacting) in a 10 eV [center-of-mass (c.m.) collision energy] collision between CS_2^+ and Xe is 1.1×10^{-13} s. The interaction length is taken to be 7 Å as established by Hasted.⁶⁰⁻⁶² The vibrational periods of CS_2^+ are 5.4×10^{-14} , 9.6×10^{-14} , and 2.8×10^{-14} s.³⁴ It is clear that the nuclear configuration of the reactant ion can change considerably during the collision, and therefore direct vertical electronic transition is an unlikely excitation mechanism. Similar timing arguments suggest that it may be more appropriate to apply the adiabatic criteria to describe electronic excitations in the CAD process. This is the topic of the next section.

B. The adiabatic criteria

When gas phase ions are collisionally activated, the resulting distribution of internal energies is often quite broad.^{1,5} It has been suggested⁵ that the peak of this distribution should be given by the adiabatic criteria of Massey.^{7,8} In this description of the collision process, the collision time is defined to be the duration of time it takes the projectile to pass through the region in which the target and the projectile are interacting. That is, the region in which the interaction potential between the target and the projectile has some reasonable fraction of its maximum magnitude

$$\tau = \frac{a}{v}, \quad (8)$$

where a is the interaction distance and v is the relative velocity of the target and the projectile. Hasted has empirically found that an interaction length of 7 Å gives the best agreement with experimental results for charge exchange type reactions.⁶⁰⁻⁶² Subsequently, 7 Å has become the accepted value for a . An excitation of energy ΔE_m will have a natural frequency associated with it

$$\nu = \frac{\Delta E_m}{\hbar}, \quad (9)$$

where $\hbar$ is Planck's constant divided by 2π , and ΔE_m is the potential energy difference between the initial state and the final state. If only the two states in question are treated, as the target and projectile interact, the system will oscillate between the character of these two states with a frequency of ν . Consequently, if the number of these oscillations during the time of interaction is large, the system can adjust to the changing conditions "adiabatically" and no transition is likely to occur, i.e., after the period of interaction, the system

will, with high probability, be in the initial state. Massey suggests that the probability of a transition to the excited state will be maximum when⁸

$$\nu\tau = \frac{\Delta E_m a}{\hbar v} \approx 1. \quad (10)$$

With regard to the experiments of Prinslow and Armentrout,⁹ consider the reaction

for which the value of $\Delta H = 4.6$ eV.

If the interaction distance is taken to be 7 Å as suggested by Hasted,⁶⁰⁻⁶² the value of ν at which the cross section maximizes is 4.91×10^6 m/s. The kinetic energy of such a collision is 6.02×10^6 eV.

This predicted maximum at 6.02×10^6 eV collision energy is nowhere near the observed maximum of 10 eV in the experimental results of Prinslow and Armentrout.⁹ Viewed from another perspective, the observed maximum in the cross section measurements can be used to estimate the width of the interaction region. At a collision energy of 10 eV, the resulting value of a is 0.009 02 Å.

This estimated interaction distance is two orders of magnitude smaller than the physical dimensions of the CS_2^+ ion, which is over 3 Å long. While there may be a maximum in the cross section for producing S^+ ions from CS_2^+ by collisionally activated dissociation with Xe near 6.02×10^6 eV collision energy, the Massey criteria, in this form, is not useful for interpreting the CAD results of Prinslow and Armentrout.⁹

de Froidmont and co-workers have taken a more modern view of the adiabatic criteria.²⁰ They recognize that the transition takes place not between the energy levels of the separated system, but between two interacting states of the system when the colliding partners are near their distance of closest approach. In the case of CAD, the reactants approach along the ground state. At some small interparticle separation, the ground state interacts with a dissociative excited state. If these states have the same symmetry, this interaction will be through an "avoided crossing." If the states have different symmetries, the interaction will be a true crossing.^{20,41} When the range of interparticle separations in which these states are interacting is given by Γ and the minimum separation of the curves in energy at the avoided crossing is given by ΔE_f , de Froidmont *et al.* define the Massey parameter ξ as

$$\xi = \frac{\Delta E_f \Gamma}{\hbar v}. \quad (11)$$

This new interpretation is displayed in Fig. 4. If ξ is large, the system can adjust itself to the changing conditions throughout the collision and the adiabatic curves are followed. This means that a transition to the dissociative excited state is unlikely. Physically, a large value of ξ implies that the states are widely separated in energy or the collision velocity is small. In either case, it is clear that the system will behave adiabatically. When the ξ parameter is small, the system tends to follow the diabatic curves and the probability of

FIG. 4. Physical interpretation of parameters used in the adiabatic criteria.

transition to the dissociative excited state is large. Of course, if the states are of different symmetries and have a true crossing, this description does not apply. Using Massey's condition that the probability of transition will maximize when $\xi=1$, together with this modern view of the adiabatic criteria, the corresponding collision velocity at which the production of S^+ by CAD maximizes is given by

$$v = \frac{\Delta E_f \Gamma}{\hbar} \quad (12)$$

Unfortunately, Γ and ΔE_f are not well-established quantities for the interaction of Xe with CS_2^+ . We can, however, make an order of magnitude approximation. In the paper by de Froidmont *et al.*, the potential curves showing avoided crossings show interaction regions typically 0.2 Å wide, suggesting that $\Gamma=0.2$ Å is a reasonable value. A similar argument suggests the value of $\Delta E_f=0.2$ eV. The kinetic energy of such a collision is 9.3 eV.

The modern interpretation of the adiabatic criteria predicts a maximum in the cross section at 9.3 eV, in excellent agreement with the experimental result of 10 eV obtained by Prinslow and Armentrout.⁹ While this result is of course serendipitous, because the values of Γ and ΔE_f are only slightly better than order of magnitude guesses, it is clear that with the improvements suggested by de Froidmont *et al.*, the adiabatic criteria gives a reasonable ballpark rule for this CAD process.

VI. CONCLUSIONS

The RRKM theory is a single state model in that it assumes the dissociation of the activated ion takes place on the ground state potential energy surface. This has been shown to be a good model from threshold up to 7.3 eV collision energy. When the anharmonicity of the highest frequency stretching vibrations is accounted for, the RRKM model describes the system well up to 7.8 eV collision energy. It is important to recognize, however, that the success of the RRKM model may be more strongly related to the fact that collisional excitations transfer energy to the reactant ion in a nonspecific way⁶³ than to rapid randomization of the excitation energy, as assumed in the development of the RRKM

theory.⁶ Such a result is a manifestation of the ambiguity of mechanistic determination owing to multiple pathways leading to the same experimental results.⁶⁴

In order to perform RRKM calculations, information about the electronic structure of the reactant ion is needed. It has been shown that the required molecular structure information, and vibrational frequencies, can be obtained with standard HF-SCF methods, although extra care may be necessary to ensure that the molecular vibrational frequencies are in accordance with the molecular symmetry.

To investigate the importance of vertical electronic excitations, Franck-Condon factors are required. Reliable estimations can be obtained for linear triatomic systems with the method of Sharp and Rosenstock.¹⁹ It has been shown that it is more appropriate to employ the Massey criteria to describe the electronic excitations involved in the CAD process analyzed here. Indeed, it has been shown, by comparison with photodissociation results, that the energy transfer in the CAD experiments does not proceed by direct electronic excitations.

ACKNOWLEDGMENT

The authors would like to express their appreciation to Professor P. B. Armentrout for supplying his experimental results.

APPENDIX

The EHT calculation was performed with the Mulliken, Wolfsberg, and Helmholtz (MWH) method as presented by McGlynn *et al.*⁶⁵ The basis atomic orbitals used were those of Clementi and Raimondi.⁶⁶ The valence orbital ionization energies were taken from McGlynn *et al.*⁶⁵ The overlap integrals were computed numerically. The Wolfsberg-Helmholtz constant was taken as the usual 1.75. As throughout this work, the values of fundamental physical constants were taken from Cohen and Taylor.⁶⁷

¹ *Collision Spectroscopy*, edited by R. G. Cooks (Plenum, New York, 1978).

² The term CAD (for collisionally activated dissociation) is synonymous with the older term CID (for collision induced dissociation). CAD is used here because it is more descriptive of the dissociation process, whereby a collisionally activated molecule undergoes unimolecular dissociation.

³ S. A. McLuckey, *J. Am. Soc. Mass Spectrom.* **3**, 599 (1992).

⁴ F. A. Lindemann, *Trans. Faraday Soc.* **17**, 598 (1922) as cited in Ref. 41.

⁵ D. M. Hirst, K. R. Jennings, J. A. Laramee, and A. K. Shukla, *Int. J. Mass Spectrom. Ion Processes* **63**, 119 (1985).

⁶ W. Forst, *Theory of Unimolecular Reactions* (Academic, New York, 1973).

⁷ H. S. W. Massey, *Proc. R. Soc. London Ser. A* **142**, 142 (1933).

⁸ H. S. W. Massey, *Rep. Prog. Phys.* **12**, 248 (1949).

⁹ D. A. Prinslow and P. B. Armentrout, *J. Chem. Phys.* **94**, 3563 (1991).

¹⁰ K. C. Kim, M. Uckotter, J. H. Beynon, and R. G. Cooks, *Int. J. Mass Spectrom. Ion Processes* **15**, 23 (1974).

¹¹ C. J. Reid, F. M. Harris, and J. H. Beynon, *Int. J. Mass Spectrom. Ion Processes* **82**, 151 (1988).

¹² C. J. Reid and F. M. Harris, *Int. J. Mass Spectrom. Ion Processes* **85**, 151 (1988).

¹³ W. B. Person, K. G. Brown, and D. Peters, *J. Phys. Chem.* **85**, 1998 (1981).

¹⁴ D. Steele, W. B. Person, and K. G. Brown, *J. Phys. Chem.* **85**, 2007 (1981).

¹⁵ S. Chin and W. B. Person, *J. Phys. Chem.* **88**, 553 (1984).

¹⁶ M. Brommer and P. Rosmus, *Chem. Phys. Lett.* **206**, 540 (1993).

- ¹⁷ M. B. Coolidge, J. E. Marlin, and J. P. Stewart, *J. Comp. Chem.* **12**, 948 (1991).
- ¹⁸ G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand-Reinhold, New York, 1950).
- ¹⁹ T. E. Sharp and H. M. Rosenstock, *J. Chem. Phys.* **41**, 3453 (1964).
- ²⁰ Y. de Froidmont, A. J. Lorquet, and J. C. Lorquet, *J. Phys. Chem.* **95**, 4220 (1991).
- ²¹ J. R. Bews and C. Glidewell, *J. Mol. Struct. Theochem.* **86**, 377 (1982).
- ²² J. H. Callomon, *Proc. R. Soc. London Ser. A* **244**, 220 (1958).
- ²³ W. J. Balfour, *Can. J. Phys.* **54**, 1969 (1976).
- ²⁴ C. R. Brundle and D. W. Turner, *Int. J. Mass. Spectrom. Ion Processes* **2**, 195 (1969).
- ²⁵ P. Coppens, J. C. Reynaert, and J. Drowart, *J. Chem. Soc. Faraday Trans. 2* **75**, 292 (1979); see also, J. Drowart, J. Smets, J. C. Reynaert, and P. Coppens, *Adv. Mass. Spectrom. A* **7**, 647 (1978).
- ²⁶ M. J. Hubin-Franskin, J. Delwiche, P. Natalis, and G. Caprace, *J. Electron Spectrosc. Relat. Phenom.* **18**, 295 (1980).
- ²⁷ A. W. Potts and G. H. Fattahallah, *J. Phys. B* **13**, 2545 (1980).
- ²⁸ L. S. Wang, J. E. Reutt, Y. T. Lee, and D. A. Shirley, *J. Electron Spectrosc. Relat. Phenom.* **47**, 167 (1988).
- ²⁹ D. D. Evard, T. Wyttenbach, and J. P. Maier, *J. Phys. Chem.* **93**, 3522 (1989).
- ³⁰ P. O. Danis, T. Wyttenbach, and J. P. Maier, *J. Chem. Phys.* **88**, 3451 (1988).
- ³¹ D. Mathur and F. M. Harris, *Mass Spectrom. Rev.* **8**, 269 (1989).
- ³² J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, and K. Draxl, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.)* **26**, 174 (1969).
- ³³ H. M. Rosenstock, D. Sims, S. S. Schroyer, and W. J. Webb, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. (U.S.)* **66**, 201 (1980).
- ³⁴ M. E. Jacox, *J. Phys. Chem. Ref. Data* **19**, 1413 (1990); see also, *ibid.* **13**, 969 (1984).
- ³⁵ G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand-Reinhold, New York, 1966).
- ³⁶ T. Koopmans, *Physica* **1**, 104 (1933), as cited in R. Daudel, G. Leroy, D. Peeters, and M. Sana, *Quantum Chemistry* (Wiley, New York, 1983).
- ³⁷ M. Miletic, D. Eres, M. Veljkovic, and K. F. Zimbov, *Int. J. Mass Spectrom. Ion Processes* **35**, 231 (1980).
- ³⁸ J. H. D. Eland and C. J. Danby, *Int. J. Mass Spectrom. Ion Processes* **1**, 111 (1968).
- ³⁹ M. W. Schmidt, K. K. Baldrige, J. A. Boatz, J. H. Jensen, S. Koseki, M. S. Gordon, K. A. Nguyen, T. L. Windus, and S. T. Elbert, *GAMESS, QCPE Bull.* **10**, 52 (1990); original program assembled by M. Dupuis, D. Spangler, and J. J. Wendoloski.
- ⁴⁰ E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations* (Dover, New York, 1980) (republished from McGraw-Hill, New York, 1955).
- ⁴¹ J. I. Steinfeld, J. S. Francisco, and W. L. Hase, *Chemical Kinetics and Dynamics* (Prentice-Hall, Englewood Cliffs, NJ, 1989).
- ⁴² M. J. Frisch, M. Head-Gordon, G. W. Trucks, J. B. Foresman, H. B. Schlegel, K. Raghavachari, M. A. Robb, J. S. Binkley, C. Gonzales, D. J. Defrees, D. J. Fox; R. A. Whiteside, R. Seeger, C. F. Melius, J. Baker, R. L. Martin, L. R. Kahn, J. J. P. Stewart, S. Topiol, and J. A. Pople, Gaussian 90, Gaussian Inc., Pittsburg, PA, 1990.
- ⁴³ Spartan version 2.0, Wave Function, Inc., 18401 Von Karman Ave., Suite 210, Irvine, CA 92715.
- ⁴⁴ Note that the smaller double-zeta 6-31G* basis set was used for the Spartan calculation because the computational platform was much slower.
- ⁴⁵ S. Califano, *Vibrational States* (Wiley, London, 1976).
- ⁴⁶ The GAMESS manual warns that the normal mode frequencies, which are produced when the VIBANL=.TRUE. flag is implemented, may not be properly symmetry adapted. From the present work, one can see that in order to obtain properly symmetry adapted frequencies, it is necessary to construct and diagonalize the full mass weighted Cartesian force constant matrix from single point energies.
- ⁴⁷ J. Momigny, G. Mathieu, H. Wankenne, and M. A. A. Ferreira, *Chem. Phys. Lett.* **21**, 606 (1973).
- ⁴⁸ J. Momigny, *J. Chim. Phys.* **77**, 725 (1980).
- ⁴⁹ G. Z. Whitten and B. S. Rabinovitch, *J. Chem. Phys.* **38**, 2466 (1963).
- ⁵⁰ S. Carter and N. C. Handy, *Mol. Phys.* **57**, 175 (1986); see also Z. Cihla and A. Chedin, *J. Mol. Spectrosc.* **40**, 337 (1971).
- ⁵¹ Orth and Dunbar (Ref. 56) have shown with double resonance ICR experiments that S_2^+ is not an observable product of unimolecular dissociation of excited CS_2^+ , but can result from the reaction of S^+ with CS_2 .
- ⁵² I. N. Levine, *Molecular Spectroscopy* (Wiley, New York, 1975).
- ⁵³ Note that any differences in w caused by assuming that the rotor has the equilibrium separation of CS^+ instead of CS are insignificant to the interpolated frequency.
- ⁵⁴ P. M. Morse, *Phys. Rev.* **34**, 57 (1929).
- ⁵⁵ G. Herzberg and E. Teller, *Z. Phys. Chem. B* **21**, 410 (1933), as cited in Ref. 19. For a general discussion, see Ref. 18.
- ⁵⁶ R. G. Orth and R. C. Dunbar, *Chem. Phys.* **45**, 195 (1980).
- ⁵⁷ M. Hamdan, F. M. Harris, and J. H. Beynon, *Int. J. Mass. Spectrom. Ion Processes* **74**, 303 (1986).
- ⁵⁸ H. Gebelein and J. Jortner, *Theor. Chim. Acta* **25**, 143 (1972).
- ⁵⁹ R. G. Gilbert and I. G. Ross, *Aust. J. Chem.* **24**, 1541 (1971).
- ⁶⁰ J. B. Hasted, *Physics of Atomic Collisions* (Butterworths, Washington, D.C., 1964).
- ⁶¹ J. B. Hasted, *J. Appl. Phys.* **30**, 25 (1959).
- ⁶² J. B. Hasted, *Adv. Electron. Electron Phys.* **13**, 1 (1960).
- ⁶³ S. Nordholm and S. A. Rice, *J. Chem. Phys.* **62**, 157 (1975).
- ⁶⁴ S. W. Benson, *The Foundations of Chemical Kinetics* (McGraw-Hill, New York, 1960).
- ⁶⁵ S. P. McGlynn, L. G. Vanquickenborne, M. Kinoshita, and D. G. Carroll, *Introduction to Applied Quantum Chemistry* (Holt, Reinhart, and Wilson, New York, 1972).
- ⁶⁶ E. Clementi and D. L. Raimondi, *J. Chem. Phys.* **38**, 2686 (1963).
- ⁶⁷ E. R. Cohen and B. N. Taylor, *Phys. Today* **41**, BG9 (1988).
- ⁶⁸ K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand-Reinhold, New York, 1979).