Carbon-13 Impurity Effect on the a_{2u} Infrared Exciton Spectrum of the Benzene Crystal*

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(Received 5 June 1972)

The C-13 shift for the a_{2u} *molecular* benzene mode has been calculated to be -0.33 ± 0.04 cm^{-1}. This confirms our previous assignment of the major pairwise molecular excitation exchange interactions for the a_{2u} vibrational exciton and enables us to pick an exciton density-of-states for the pure crystal. We also calculate the natural-abundance isotopically mixed benzene crystal density-of-states and its spectrum. Predicted in-band spectral resonances are consistent with published experimental data and facilitate their interpretation in terms of Davydov components, density-of-states peaks, band center, site shift, and exciton interactions. The implications and applications of the C-13 presence in "pure crystal" spectra are discussed.

INTRODUCTION

The benzene crystal has played an important role in our understanding of Frenkel excitons.[1] Considering vibrational excitons, the out-of-plane ("umbrella") a_{2u} mode has been of most interest, due to its high ir intensity,[2] its large exciton bandwidth, and its history[3] of assignments and misassignments. Recently new experimental data, including polarizations, have been obtained.[6]

Amazingly, for a molecule that has often been used as the classical example for the analysis of molecular vibrations,[7] the isotopic C-13 shift of the only a_{2u} mode of benzene has been recently under dispute.[3,5–8] Values from 0 to 4 cm^{-1} have been quoted[8,9a] and this dispute has had its feedback on the problem of "resonance pairs" in C_6H_6 doped C_6D_6 crystals.[3,8]

In this work we have first calculated the a_{2u} C-13 shift and found it to be 0.33 cm^{-1}. This result corroborated our previous assignment of resonance pairs[3] and the general validity of the exciton density-of-states function which we calculated before for the *idealized* pure benzene crystal (no C-13 content). Furthermore, it enabled us to calculate the spectral features for the *real*, natural abundance "neat" crystal. This calculation seems to solve some of the previous mysteries concerning the assignment of the Davydov components. It also serves as an example *par excellence* for in-band resonances[9b] due to isotopic impurities and clarifies the influence of the latter on the width of the Davydov components.

All crystals of benzene which are currently available contain about 6% mole of $^{13}C^{12}C_5H_6$ due to the 1.1% ^{13}C isotope abundance in nature. Consequently, spectral features of crystalline benzene such as the broadness and splittings of Davydov components must be considered with regard to the effect of the $^{13}C^{12}C_5H_6$ impurity on them, in contrast to what would be observed if one had an isotopically pure crystal. We have attempted to determine the effect of the $^{13}C^{12}C_5H_6$ impurity on the $\nu_{11}(a_{2u})$ vibrational exciton band of benzene by assuming that the $^{13}C^{12}C_5H_6$ represents a dilute impurity in the crystal.

The problem of an impurity in a crystal and its effects on lattice vibrations and electronic states has been studied by many workers. Fundamental work on the subject was done by Lifshitz[10] who considered the effect of localized perturbations in a system with a continuous energy spectrum, and by Koster and Slater,[11–13] who applied a Green's function method to the study of the effect of an impurity on the electronic states of a metal. We have utilized the method of a single particle Green's function in terms of the Green's function of a crystal of pure benzene. The formalism is developed in a review paper by Izyumov[14] and has been used by Sommer and Jortner[15,16] in their work on isotopic impurities in molecular crystals.

TABLE I. Frequencies and intensities of $E_j(0)$ for the C_6H_6 ν_{11} vibrational exciton band.[a]

j	$E_j(0)$ (cm^{-1})	$M^2(j)$	Polarization (crystal axis)
1	−17.2	0.50	a
2	−15.6	0.45	c
3	10.0	0.05	b

[a] References 2 and 9.

We have shown that more than one extra spectral peak may result from a low concentration in-band impurity (like C-13). Specifically, in this case, we can identify one extra peak in the spectrum as being due to the C-13, and show that the others correspond to the three allowed Davydov components in the pure C-12 crystal (which has never been investigated experimentally). The C-13 peak is also used for closer identification of the center-of-the-exciton-band, thereby enabling a more accurate location of the forbidden

Davydov component, as well as determination of the exciton pairwise interactions, the density of states and the dispersion relation. We also show the influence of the C-13 impurity on the broadening and depolarization of the Davydov components in the "neat" (natural abundance) benzene crystal.

METHOD

The optical spectrum of the impurity-doped benzene crystal, $d(E)$, was calculated from the expression for optical density given by Herzenberg and Modinos,[17] and by Sommer and Jortner[15,16]:

$$d(E)=\pi^{-1}\,\mathrm{Im}\sum_n\sum_m\sum_\alpha\sum_\beta \mathbf{u}_{n\alpha}\mathbf{u}_{m\beta}G_{n\alpha,m\beta}. \qquad (1)$$

$G_{n\alpha,m\beta}$ is the Green's function for the mixed crystal in terms of the crystal states in the localized basis, $|n\alpha\rangle$ and $|m\beta\rangle$, where n and m are primitive cell indices and α and β are site indices. The transition dipole moment between the ground and excited molecular states at site $n\alpha$ is given by $\mathbf{u}_{n\alpha}=\langle 0\,|\,u\,|\,n\alpha\rangle$, where u is the electric dipole operator. Through use of Dyson's equation, Eq. (1) can finally be expressed as

$$d(E)=d^0(E)+\sigma^{-1}L(E)T(E), \qquad (2)$$

where $d^0(E)$ is the optical density of the pure crystal,

$$d^0(E)=[N\sum_j M(j)]\{M(j)\delta[E-E_j(0)]\}, \qquad (3)$$

$M(j)$ is the transition moment per *primitive cell* of the jth exciton branch of the pure crystal and $E_j(0)$ is the frequency of the Davydov component associated with the jth exciton branch; the contribution of the single impurity to the optical density is given by the second expression on the rhs of Eq. (2), where σ is the number of molecules per primitive cell, in the case of benzene equal to four. Also,

$$T(E)=\sum_j M(j)^2/[E-E_j(0)]^2, \qquad (4)$$

and

$$L(E)=g_0(E)U_0^2/\{[1-U_0F(E)]^2+\pi^2U_0^2g_0(E)^2\}, \qquad (5)$$

where $g_0(E)$ is the density of states of the pure crystal at frequency E, and U_0 is the local perturbation of the impurity molecule ("trap-depth"), equal in our case to the difference in the frequency of the ν_{11} vibrations in the C_6H_6 and $^{13}C^{12}C_5H_6$ molecules. $F(E)$ is defined by the integral

$$F(E)=P\int[g_0(E')dE'/(E-E')]. \qquad (6)$$

If the concentration C of the impurity is finite but low, the factor σ^{-1} in Eq. (2) can be replaced by the number of impurities σNC. Thus, for the dilute impurity case ($C\ll 1$), Eq. (2) becomes

$$d(E)=d^0(E)+NCL(E)T(E). \qquad (7)$$

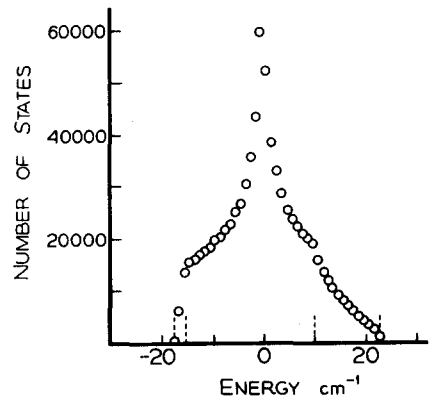

FIG. 1. $a_{2u}(\nu_{11})$ exciton band. $M_a=M_b=M_c=0$, $M_{\mathrm{I\,II}}=0.7$, $M_{\mathrm{I\,III}}=4.1$, $M_{\mathrm{I\,IV}}=0.9$. [From J. C. Laufer and R. Kopelman, J. Chem. Phys. **53**, 3674 (1970).]

In our calculation, we used Eq. (7) to calculate the effect of the $^{13}C^{12}C_5H_6$ impurity on the pure C_6H_6 spectrum. We took $C=0.06$. The positions and intensities of the Davydov components, $E_j(0)$, are taken from the work of Hollenberg and Dows,[2] and are listed in Table I. For convenience, the total optical density of the spectrum was normalized, $\sum_j M(j)=1$, and the $M(j)^2$'s were assigned values proportional to the relative intensities of their respective branches. The density-of-states functions, $g_0(E)$, have been previously calculated by us for various vibrational excitons.[8] Using the same method, we recalculated $g_0(E)$ for the present band to a resolution of 0.9 cm^{-1} with a mesh of 195 112 wave vectors. The input data was identical with that given in Fig. 3 of Ref. 8, which is reproduced here in Fig. 1. The value of U_0 was determined to be -0.33 cm^{-1} by means of a normal mode calculation on the $^{13}C^{12}C_5H_6$ molecule. The Appendix gives the details of this calculation. It should be noted that using as input data Fig. 1 or Fig. 2 of Ref. 8, instead of Fig. 3, would not appreciably alter our results (see below). Our most suspect step is the utilization of Eq. (7) for a concentration as high as 6%.

DISCUSSION

The calculation of the C-13 shiftf(for $^{13}C^{12}C_5H_6$) of the molecular $a_{2u}(\nu_{11})$ mode confirms the assignments of Brodersen *et al.*[9a] and of Marzocchi *et al.*,[6] but disagrees with the much larger value of Bernstein,[5] i.e., his spectral assignment of the 694.1 cm^{-1} mode to $^{13}C^{12}C_5H_6$. This enables us to retain the previous assignment by one of us[3] of the 693.5 cm^{-1} band observed by Hall[4] as a "resonance pair" band, in agreement with the earlier assignment by Hollenberg and Dows[2] of their

TABLE II. G matrix for nonplanar vibrations

	S_{11}	S_4	S_5	S_{16a}	S_{17a}
S_{11}	$\mu_H+\frac{1}{6}P$	$-\frac{2}{3}G$	$\frac{1}{6}G(1+4\rho)$	$2H/(6)^{1/2}$	$[H/2(6)^{1/2}](1+3\rho)$
	S_4	$8P$	$-(4\sqrt{3}P/6)(1+4\rho)$	$-24J/(18)^{1/2}$	$[-6J/(18)^{1/2}](1+3\rho)$
		S_5	$\mu_H+\frac{1}{6}P(1+4\rho)^2$	$[2J/(6)^{1/2}](1+4\rho)$	$[J/2(6)^{1/2}](1+3\rho)(1+4\rho)$
			S_{16a}	$4B$	$B(1+3\rho)$
				S_{17a}	$\mu_H+\frac{1}{4}B(1+3\rho)^2$
					S_{16b}

m = mass of hydrogen atom

M = mass of carbon isotope

$C=r_0/R_0=\dfrac{\text{C-H equilibrium distance}}{\text{C-C equilibrium distance}}$

$\mu_H=m^{-1}$

$P=M_1^{-1}+M_2^{-1}+M_3^{-1}+M_4^{-1}+M_5^{-1}+M_6^{-1}$

$B=M_2^{-1}+M_3^{-1}+M_5^{-1}+M_6^{-1}$

$D=(4/M_1)+M_2^{-1}+M_3^{-1}+(4/M_4)+M_5^{-1}+M_6^{-1}$

$J=M_2^{-1}+M_3^{-1}-M_5^{-1}-M_6^{-1}$

$M=(4/M_1)-M_2^{-1}+M_3^{-1}-(4/M_4)+M_5^{-1}-M_6^{-1}$

$H=-M_2^{-1}+M_3^{-1}-M_5^{-1}+M_6^{-1}$

$I=-(2/M_1)+M_2^{-1}+M_3^{-1}-(2/M_4)+M_5^{-1}+M_6^{-1}$

$L=-M_2^{-1}+M_3^{-1}+M_5^{-1}-M_6^{-1}$

$G=M_1^{-1}-M_2^{-1}+M_3^{-1}-M_4^{-1}+M_5^{-1}-M_6^{-1}$

694.3 and 693.5 cm^{-1} bands to "remnants of the correlation coupling." The resulting $M_{I\,III}$ interaction is in the range of 2.8–4.0 cm^{-1}. This should be compared to the values of 2.8–4.1 cm^{-1} derived from Davydov components.[2,3,6,18,19] The difficulty of assigning such Davydov components, due to $^{13}C^{12}C_5H_6$ impurity bands, is discussed below.

We have plotted the optical density spectra of the $^{13}C^{12}C_5H_6$ impurity, as defined by $CL(E)T(E)$ of Eq. (7), in Fig. 2. In this figure, the three optically allowed exciton branches, with polarizations parallel to the crystal axes **a**, **b**, and **c**, are shown separately. In the single impurity formulation of Eq. (2), the Davydov components of the pure crystal are taken to be delta functions of infinitely narrow bandwidth at energies $E_j(0)$. The question then arises as to the possibility that the broadness of the Davydov components in the real crystal (3–10 cm^{-1} in half-width) is caused by the impurity. Hoshen and Jortner[20] have derived a simple expression for the impurity broadening in the case we are concerned with, where $U_0 \ll W$, i.e., the trap depth U_0 is much smaller than the width W of the exciton band. The impurity broadening of the jth

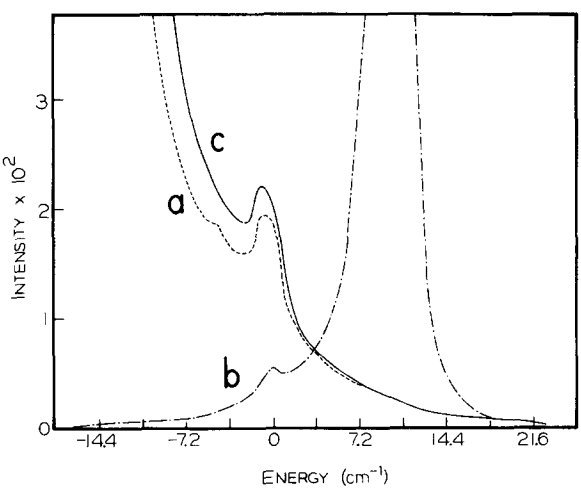

FIG. 2. Calculated C-13 impurity induced absorption in the benzene a_{2u} vibrational exciton band for the three crystal polarizations. Molecular exciton data are from "set 3" of Ref. 9. Note that only one side of the **a** and **c** absorption peaks is shown here. Note also that the "intensity" is only an order of magnitude indication and that it has been normalized so that the total pure crystal intensity is unity.

of the carbon isotopes of benzene.

S_{16b}	S_{17a}	S_{10a}	S_{10b}
$2I/3\sqrt{2}$	$(I/6\sqrt{2})(1+3\rho)$	$[J/2(6)^{1/2}](1+\rho)$	$(K/6\sqrt{2})(1+\rho)$
$-8K/(6)^{1/2}$	$[-2K/(6)^{1/2}](1+3\rho)$	$(-2H/\sqrt{2})(1+\rho)$	$[-2I/(6)^{1/2}](1+\rho)$
$(2K/3\sqrt{2})(1+4\rho)$	$(K/6\sqrt{2})(1+3\rho)(1+4\rho)$	$[H/2(6)^{1/2}](1+\rho)(1+4\rho)$	$(I/6\sqrt{2})(1+\rho)(1+4\rho)$
$4H/\sqrt{3}$	$(H/\sqrt{3})(1+3\rho)$	$L(1+\rho)$	$(J/\sqrt{3})(1+\rho)$
$(H/\sqrt{3})(1+3\rho)$	$(H/4\sqrt{3})(1+3\rho)^2$	$\frac{1}{4}L(1+\rho)(1+3\rho)$	$(J/4\sqrt{3})(1+\rho+3\rho^2)$
$\frac{4}{3}D$	$\frac{1}{3}D(1+3\rho)$	$(J/\sqrt{3})(1+\rho)$	$\frac{1}{3}M(1+\rho)$
S_{17b}	$\mu_H+(D/12)(1+3\rho)^2$	$(J/4\sqrt{3})(1+\rho+3\rho^2)$	$(M/12)(1+3\rho)(1+\rho)$
	S_{10a}	$\mu_H+\frac{1}{4}B(1+\rho)^2$	$(H/4\sqrt{3})(1+\rho)^2$
		S_{10b}	$\mu_H+(D/12)(1+\rho)^2$

exciton branch, $Y(j)$, is a function only of U_0 and the impurity concentration C_A:

$$Y(j)=|U_0|(C_AC_B)^{1/2}. \tag{8}$$

Taking $C_A=0.06$ and $C_B=1-C_A$, we see that $Y(j)$ is only about 0.1 cm^{-1}. Therefore the C-13 impurity is *not* responsible for the broadening of the Davydov components of the real crystal. The broadness of the impurity spectra shown in Fig. 2 exists only near the baseline and does not contribute significantly to the half-width of any Davydov component.

Near the band center, at 0 cm^{-1}, three maxima are observed in the impurity spectra, one in each polarization. Because of the factor $[E-E_j(0)]^{-1}$ in $T(E)$ of Eq. (7), the three maxima are not coincident. As long as $E_j(0)$ is not so close to the band center that its optical density half-width encompasses the latter, it is expected that one or more impurity induced "resonance" absorption peaks may appear in a crystal spectrum of a particular molecular state. Marzocchi, Bonadeo, and Taddei[6] have published polarized ir spectra of crystalline benzene showing several absorbances in the ν_{11} band which cannot be assigned to Davydov components. They assign a depolarized peak at 688.5 cm^{-1} to the $^{13}C^{12}C_5H_6$ impurity, and a polarized peak at 691 cm^{-1} to a "refractive index dispersion effect between the sharp ^{13}C band (at 688.5 cm^{-1}) and the strong and broad ^{12}C band." In view of our impurity calculations (Fig. 2), it is reasonable to assign the 688.5 peak to at least two of the three ^{13}C peaks expected to be present in the crystal spectra of the band. The coincidence of these impurity peaks would then account for the observed depolarization. The peak at 691 cm^{-1} may then be assigned as another ^{13}C absorption.

There are several interesting apparent discrepancies between current naive theories of mixed crystals and the spectra of Marzocchi *et al.*[6] The fact that the trap depth, U_0, of the ^{13}C impurity is much smaller than the bandwidth of the C_6H_6 ν_{11} mode leads to the expectation that there should not be any impurity modes as such.[20] However, the single impurity model which we have employed does predict an intensity contribution from the impurity, albeit with probably unreliable optical densities. The experimental spectra do show peaks

TABLE III. Frequencies of the out-of-plane vibrations of $^{12}C_6H_6$ and $^{13}C^{12}C_5H_6$.

Mode	$^{12}C_6H_6$ (cm^{-1})	$^{13}C^{12}C_5H_6$ (cm^{-1})
ν_{11}	672.854	672.529
ν_4	992.06	991.21
ν_5	705.81	702.10
ν_{17a}	983.82	983.82
ν_{16a}	404.17	404.17
ν_{17b}	983.82	979.68
ν_{16b}	404.17	400.37
ν_{10a}	850.95	850.95
ν_{10b}	850.95	848.69

assigned to the impurity that look almost as strong as the weakest of the Davydov components. (However, one should beware of the apparent intensity of a satellite band.) Another fact is that the mixed crystal data[2,4,5] on the ν_{11} band in benzene seem to put the band center at 697 cm^{-1}. The impurity induced peaks, if they can be observed, are expected to be located very close to the band center. However, an explanation exists for the "shift" of these peaks to about 690 cm^{-1} in the spectra of Marzocchi *et al.*[6] Bernstein,[5] in his investigation of various isotopic benzene systems, points out an anomaly in the ν_{11} "site shift" of 23.9 cm^{-1} obtained from a C_6H_6 doped C_6D_6 host. This system may not be an[1] "ideal mixed crystal." Using as guests C_6H_5D, $C_6H_5D_2$ (*p* and *m*), $C_6H_3D_3$, and C_6D_5H gives values of 14–18 cm^{-1}, i.e., a shift of about 8 cm^{-1} less. This would actually put the band center at about 687–691 cm^{-1}, in very good agreement with the location of the ^{13}C induced bands. We see therefore that ^{13}C induced resonances (for $U_0 \ll W$) may serve as a new, improved criterion for the location of the exciton band center, and thus also for the determination of the site shift.

Our above experience with the ν_{11} benzene exciton band should serve as a warning about investigations of so-called pure crystals. Obviously, many of the literature disagreements concerning the location of the Davydov components of this exciton band,[2,3,6,18,19,21] and therefore the correct values of the exciton interaction parameters,[3,8,19] can now be straightened out. Specifically it seems, both from the dimer assignment (see above) and the Davydov component assignment (see above), that the most reasonable ν_{11} exciton parameters are the first two sets listed by us previously.[8] The appropriate density-of-states for set 2 which agrees with Marzocchi *et al.*,[6] is given in Fig. 1 (taken from Fig. 3 of our previous paper[8]).[22] We see, therefore, that C-13 *induced* bands may be a useful spectroscopic tool. There is obviously still a need for more theoretical and experimental work on impurity modes in the benzene crystal.

CONCLUSION

Since the trap depth of the $^{13}C^{12}C_5H_6$ ν_{11} vibration with respect to the $^{12}C_6H_6$ ν_{11} mode is only -0.33 cm^{-1}, the ^{13}C state is situated within the $^{12}C_6H_6$ band. According to calculations based on mixed crystal theory, the impurity concentration of 6% is not expected to significantly broaden the Davydov components of a pure $^{12}C_6H_6$ crystal ν_{11} exciton band. Our calculations with a single particle Green's function model show however, that absorptions attributable to the impurity are expected to be present in the neat crystal spectrum. In the polarized spectra of the ν_{11} band of the benzene crystal by Marzocchi *et al.*, which show a peak assigned to the ^{13}C impurity and another peak 2.5 cm^{-1} away, of different polarization, attributed to a refractive index effect, we assign both peaks as impurity induced. These assignments provide us with a new improved value for the site shift (15–18 cm^{-1}) and confirm our previously derived principal exciton interaction and the exciton density-of-states. C-13 in-band resonances are potentially useful tools in the investigation of energy bands in molecular crystals, vibrational as well as electronic (i.e., the first excited singlet).

APPENDIX

U_0 was determined from the difference in frequency between the ν_{11} mode of $^{12}C_6H_6$ and the ν_{11} mode of $^{13}C^{12}C_5H_6$. The ν_{11} frequencies were obtained by doing a **GF** normal coordinate calculation[7] on each molecule. The calculation was modelled on the earlier calculation of Miller and Crawford[23] for the nonplanar vibrations of benzene, and we used their choice of symmetry coordinates and **F** matrix. The values of the **F** matrix elements were taken from the later work of Whiffen.[24] We derived the **G** matrix for the nonplanar vibrations of the carbon isotopes of benzene; it is shown in Table II. The eigenvalue problem was solved by an iterative search subroutine on the CDC 6600 computer of the University of Minnesota. Table III lists the frequencies of the nonplanar vibrations of $^{12}C_6H_6$ and $^{13}C^{12}C_5H_6$ obtained from the calculations.

* Supported by PHS Grant NB-08116; presented at 26th Molecular Structure and Spectroscopy Symposium, Ohio State University, Columbus, Ohio, paper C4, June 1971.

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of Bernstein[5] and the 694.3 cm^{-1} feature of Hollenberg and Dows,[2] and also in agreement with the neat crystal spectra, provided that the center-of-band is put at 692 cm^{-1} (see below).
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THE JOURNAL OF CHEMICAL PHYSICS VOLUME 57, NUMBER 8 15 OCTOBER 1972

Kinetic Energy Release in the Dissociation of Some Simple Molecular Ions. Water and Hydrogen Sulfide

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(Received 29 June 1972)

The technique of ion kinetic energy spectroscopy has been applied to a study of $S^{+\cdot}$ formation from $H_2S^{+\cdot}$ and $O^{+\cdot}$ formation from $H_2O^{+\cdot}$. Unimolecular formation of $S^{+\cdot}$ occurs by predissociation of the first excited state via the repulsive $^4A_2$ state of $H_2S^{+\cdot}$. Above the classical crossover region this reaction proceeds rapidly on the mass spectrometer time scale but tunneling through the barrier occurs slowly and gives rise to metastable ions which fragment with conversion of all the available potential energy to kinetic energy. Collisional excitation of ground state $H_2S^{+\cdot}$ yields excited ions which rapidly dissociate via the $^4A_2$ repulsive surface to give substantially excited $(v=2)H_2$. This reaction occurs with the partitioning of some 30% of the available energy into translational energy of the products. The heat of formation of $S^{+\cdot}$, determined from the appearance potential, requires only slight correction for the excess energy term arising from the potential energy difference between the crossover region and the ground state of the products because the repulsive surface is unusually flat. Ground state $H_2O^{+\cdot}$ ions undergo collision-induced excitation with loss of 22 ± 4 eV of kinetic energy to give a high energy excited state which fragments directly to give $O^{+\cdot}(^2D$ or $^2P)$ and vibrationally excited H_2. Appearance potential measurements do not provide a reliable assignment of the products because of the excess energy terms. These results are in contrast to earlier conclusions that fragmentation upon electron impact yields two hydrogen atoms.

INTRODUCTION

The kinetic energy (T) acquired by the fragments when a molecular ion dissociates offers a means of probing unimolecular reactions.[1] It is advantageous to study simultaneously the related process of collision-induced fragmentation and to measure both the kinetic energy (T) released upon reaction and the kinetic energy (Q') lost[2] by the reactant ion in these collisional processes. In small molecular ions, where excited states are well separated and where at least some thermochemical data for these states are available, unimolecular[3] and collision-induced[4] dissociation studies can be combined for a better understanding of the nature of fragmentation reactions as well as the thermochemistry of the system. The type of question which can be addressed is as follows: (i) does a particular reaction occur by predissociation? (ii) what is the approximate energy of the reactant state? (iii) is the kinetic energy release consistent with the formation of ground state products?

Reactions (1) and (2) have been chosen for study by this method,

$$H_2S^{+\cdot}\longrightarrow S^{+\cdot}+H_2(2H), \quad (1)$$

$$H_2O^{+\cdot}\longrightarrow O^{+\cdot}+H_2(2H), \quad (2)$$

both because of the intrinsic practical and theoretical