

## Photon-stimulated desorption of solid neopentane

J. A. Kelber

*Sandia National Laboratories, Albuquerque, New Mexico 87185*R. R. Daniels, M. Turowski,\* and G. Margaritondo  
*University of Wisconsin—Madison, Madison, Wisconsin 53706*

N. H. Tolks†

*Bell Communication Research, Incorporated, Murray Hill, New Jersey 07974*

J. S. Kraus

*AT&T Bell Laboratories, Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey 07974*

(Received 13 April 1984)

The positive-ion yields and kinetic-energy distributions resulting from the photon bombardment of solid neopentane  $[(\text{CH}_3)_4\text{C}]$  have been measured for photon excitation energies between 17 and 45 eV. The ion ( $>94\%$   $\text{H}^+$ ) appearance potential is at  $20 (\pm 1)$  eV with a yield maximum at  $24 (\pm 1)$  eV of  $2 \times 10^{-7}$  ions/photon. For all photon energies, the ion-kinetic-energy distribution peaks at  $1.9 (\pm 0.25)$  eV and is broadened asymmetrically to higher kinetic energies. These results indicate that the process responsible for  $\text{H}^+$  desorption near threshold is a  $\text{C } 2s \rightarrow \text{Rydberg-type level excitation}$  followed by decay to a final state involving several valence holes and at least one electron in a Rydberg-type level.

## I. INTRODUCTION

The low-energy ( $<1000$  eV) electron- and photon-stimulated desorption (ESD and PSD, respectively) of ions and neutrals from condensed organic materials has been the subject of a number of recent investigations.<sup>1-5</sup> These studies have shown that ion desorption, mainly  $\text{H}^+$ , results from the creation of states with two or more valence holes. More specifically, studies of hydrocarbon and fluorocarbon molecular solids<sup>4,5</sup> have demonstrated that such states are localized within functional groups (e.g.,  $-\text{CH}_3$ ) of the molecule. An unresolved question, however, is the extent to which such multihole states are associated with electrons in bound levels which lie above the highest ground-state-occupied orbitals (e.g., Rydberg orbitals). Since such "excitonlike" states may cause the desorption of electronically excited neutrals as well as ions, this question is of technological as well as scientific interest for hydrocarbons and related materials. For example, protons and atomic hydrogen with greater than thermal ( $\sim 1$  eV) kinetic energy are generally believed to play important roles in polymer degradation processes resulting from polymer exposure to ionizing radiation.

In the extensively investigated dissociation of gas-phase methane,<sup>6-9</sup> it has been demonstrated that either the direct creation of the  $(1t_2^{-2}, 3a_1^1)$  state<sup>9</sup> or autoionization following a  $2a_1 \rightarrow 3a_1$  Rydberg excitation results in the production of both  $\text{H}^+$  and  $\text{H}^*$  (electronically excited neutral atomic hydrogen) with kinetic energies of  $\sim 1.5-4.5$  eV.<sup>6-8</sup> The excitation of a "bare" multihole state in gas-phase  $\text{CH}_4$ , the approach to which is marked by the production of both  $\text{H}^+$  and very high Rydberg  $\text{H}^*$  [ $n > 20$  (Refs. 7 and 8)] produces species with kinetic energies of

$\sim 8$  eV or more.<sup>7,8</sup> These results are in accord with recent theoretical studies which indicate that a bare two-hole state in methane ( $1t_2^{-2}$ ) will produce  $\text{H}^+$  with kinetic energies of  $\sim 10$  eV, while a particular excitonlike state ( $1t_2^{-2}, 3a_1^1$ ) will result in  $\text{H}^+$  kinetic energies of 4 eV.<sup>10</sup> The reason for this reduction in kinetic energy is that, as one would expect, hole-hole repulsion is partially reduced by the screening electron.<sup>10</sup> Therefore by measuring the kinetic energy of ESD- or PSD-produced  $\text{H}^+$  from a hydrocarbon surface, one may infer whether the final predisociative state is a bare multihole state of a multihole-electron excitation.

In comparing the  $\text{H}^+$  produced from an organic surface to that produced from the dissociation of gas-phase methane, we have chosen to examine solid neopentane  $[(\text{CH}_3)_4\text{C}]$ . This system has been well characterized by previous ESD studies which show that multihole states which produce  $\text{H}^+$  are localized on  $-\text{CH}_3$  groups.<sup>4</sup> Thus the dissociation processes should be similar to those observed for  $\text{CH}_4$ .

## II. EXPERIMENT

The measurements reported here were carried out on the stainless-steel Seya-Namioka beam line at the University of Wisconsin Synchrotron Radiation Laboratory (Stoughton). With this beam line, the photon energy could be varied between 10 and  $\sim 45$  eV, although second-order radiation made measurement at energies less than  $\sim 17$  eV extremely difficult. The base pressure of the vacuum system was  $\sim 1 \times 10^{-10}$  Torr. Neopentane, more than 99.8% pure, was obtained from a commercial source and used without further purification. The neo-

pentane was condensed from a doser tube onto an Ag or Cu substrate at pressures of  $\sim 3 \times 10^{-8}$  Torr for exposure times of  $\sim 3$  min. The temperature of the substrate during dosing and PSD measurements was  $\sim 30$  K but would be raised to  $\sim 500$  K for cleaning. These dosing parameters have previously been shown to result in the deposition of thin films which do not charge under exposure to ionizing radiation.<sup>4,5</sup> To observe possible charging effects in our experiments, the position and shape of ion-kinetic-energy distribution curves (IEDC's) were observed as the photon flux was varied. In some cases, after long dosing times, the IEDC's were observed to shift to higher kinetic energies at full flux (i.e., the slits in the beam line were wide open), indicating that thick films charged positively. In the data reported here, no shifts were observed.

Ions were detected using a commercially available double-pass cylindrical mirror analyzer (CMA) with standard pulse-counting electronics. The CMA was operated in a constant-pass energy mode (62.5 eV), with the inner cylinder and retarding grid at the same potential. The details of using such an instrument to detect positive ions have been presented elsewhere.<sup>11</sup> Since time-of-flight methods were not employed in this experiment, the ion flux from the surface was not mass analyzed.<sup>11</sup> However, ESD studies on solid neopentane have established that the only observable cation products at excitation energies

$< 110$  eV, are  $H^+$ ,  $H_2^+$ , and  $CH_3^+$ .<sup>4</sup> At excitation energies between 20 and 50 eV, the conditions relevant to our studies, the combined  $H_2^+$  and  $CH_3^+$  yield is  $< 6\%$  of the total ion yield.<sup>4,12</sup> Ion flux from a clean substrate was found to be negligible compared to that observed for a substrate exposed under the conditions described above, indicating that effectively all the ions observed in our measurements originated from the neopentane overlayer and not from the metal substrate.

The ion yield per photon as a function of photon excitation energy ( $\hbar\omega$ ), shown in Fig. 1, was obtained by integrating the area of each IEDC and dividing by the photon flux. This latter quantity was determined by measuring the photoelectron yield from an 85% transmission tungsten mesh placed in the beam path and dividing by the known tungsten emission efficiency as a function of photon wavelength. Since the combined effects of sublimation and beam damage were observed to lead to an exponential decay of signal with time at constant  $\hbar\omega$ , the ion yield per photon was corrected by an exponential time decay factor to give a normalized ion yield. This correction did not result in any major modification of features in the ion-yield curve. At maximum, a yield of  $2 \times 10^{-7}$  ions/photon was observed, which is comparable to that obtained in other PSD experiments.<sup>1</sup>

In comparing IEDC's obtained from a surface to those reported from gas-phase measurements, we note that the gas-phase kinetic energies are all reported relative to the vacuum level of the molecule. In measuring the energies of ions desorbed from a surface, the Fermi levels of the spectrometer and the metal substrate are the same (see Fig. 2). The kinetic energy of a particle relative to the vacuum level of the sample ( $E_{kin}^{vac}$ ) is equal to the observed kinetic energy ( $E_{kin}^{obs}$ ) plus the difference between detector and sample work functions ( $\phi_D$  and  $\phi_S$ ), respectively,

$$E_{kin}^{vac} = E_{kin}^{obs} + \phi_D - \phi_S. \quad (1)$$

$\phi_D$  was obtained by measuring, at a given  $\hbar\omega$ , the kinetic energy of electrons ejected from the Fermi level of the Ag substrate and was found to be  $5.25 (\pm 0.1)$  eV.  $\phi_S$  can be approximated from photoemission experiments on gas-

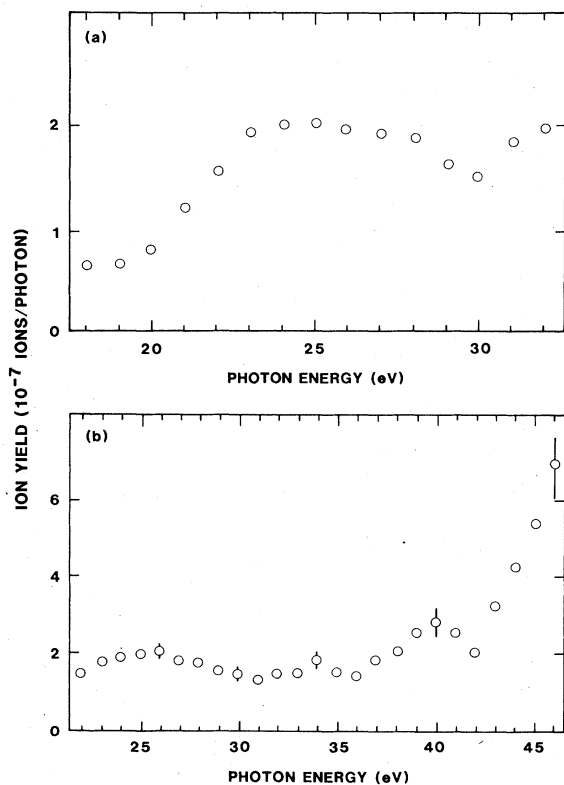


FIG. 1. Normalized ion yield for photon-stimulated desorption from solid neopentane [(CH<sub>3</sub>)<sub>4</sub>C]. (a) The near-threshold region. (b) For  $21 \leq \hbar\omega \leq 46$  eV. Error bars increase as the photon flux falls off for  $\hbar\omega > 30$  eV. Data for (a) and (b) are from different runs.

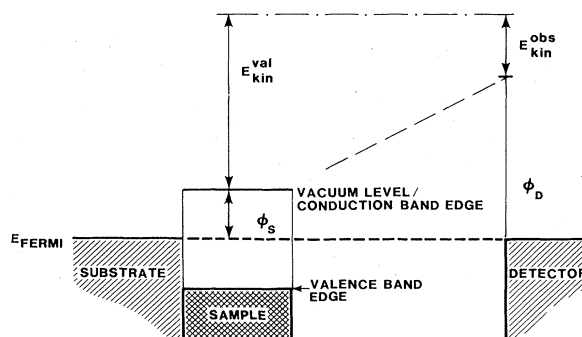


FIG. 2. Energy diagram for measurement of ion-kinetic energies for adsorbates on metal substrates.

phase and solid hydrocarbon thin films<sup>13</sup> and photoemission threshold measurements of polyethylene<sup>14</sup> as 4.5 ( $\pm 0.25$ ) eV. The correction factor [Eq. (1)] is therefore 0.7 ( $\pm 0.25$ ) eV. The uncertainty in this correction factor is the major source of uncertainty in the energies of the peaks in the IEDC's.

### III. RESULTS AND INTERPRETATION

The normalized ion yield, Fig. 1, for  $\hbar\omega \leq 30$  eV, was consistently reproduced in all our runs and is quite similar to that obtained by Rosenberg *et al.*<sup>1</sup> for H<sup>+</sup> desorbed from solid CH<sub>3</sub>OH, in which all the desorbed H<sup>+</sup> originates from the -CH<sub>3</sub> group. The similarity of our results to those of Rosenberg *et al.*<sup>1</sup> indicates that desorption of H<sup>+</sup> from -CH<sub>3</sub> groups in different molecules occurs by a similar process. The 20 ( $\pm 1$ )-eV threshold in the ion yield from solid neopentane (Fig. 1) is quite close to the C 2s photoemission threshold observed for a variety of hydrocarbon molecular solids in x-ray excited photoemission experiments.<sup>15</sup> This confirms previous ESD results which show that excitations leading to ion desorption result from an initial excitation of the C 2s shell.<sup>4,5</sup> The PSD ion appearance potential, 20 ( $\pm 1$ ) eV (Fig. 1), differs from the H<sup>+</sup> appearance potential of 25 ( $\pm 1$ ) eV reported for the ESD studies.<sup>4</sup> The reason for this difference is that the electron excitation energy reported in the ESD studies corresponds to the applied voltage difference between the Fermi levels of the substrate and cathode, corrected for the cathode work function and temperatures of the thermionic emitter.<sup>4</sup> The electrons emitted by the cathode may finally be located in the bottom of the sample conduction band (nearly degenerate with the vacuum level for most hydrocarbons<sup>13-15</sup>) or, for very thin films, may tunnel to the substrate Fermi level. An electron which is finally located in the sample conduction band should deliver an excitation energy ( $E$ ) to the system given by

$$E = V - \phi_S, \quad (2a)$$

where  $V$  is the applied potential and  $\phi_S$  the sample work function. For photons, we simply have

$$E = \hbar\omega. \quad (2b)$$

Therefore, ESD and PSD appearance potentials should differ by  $\phi_S$ . For solid neopentane, the ESD and PSD thresholds differ by 5 ( $\pm 2$ ) eV, which compares well to the nominal  $\phi_S$  value of 4.5 eV.<sup>14</sup>

While the normalized ion yield (Fig. 1) displays additional maxima near 34 and 40 eV, these features were not consistently reproduced in our experiments, although a minimum near 30 eV was always observed. The reason for this uncertainty is the low photon flux for  $\hbar\omega > 30$  eV, so that small uncertainties in the photon flux produce large uncertainties in the normalized yield. Therefore, while the normalized yield does increase for  $\hbar\omega > 30$  eV, the energies of any maxima in this region are unknown.

The IEDC's (Fig. 3) consistently display a major peak near 1.9 ( $\pm 0.25$ ) eV, with a smaller broad feature centered near 3.5 eV and some ion intensity out to  $\sim 7$  eV. These data resemble those reported by Madden *et al.*<sup>16</sup> for the

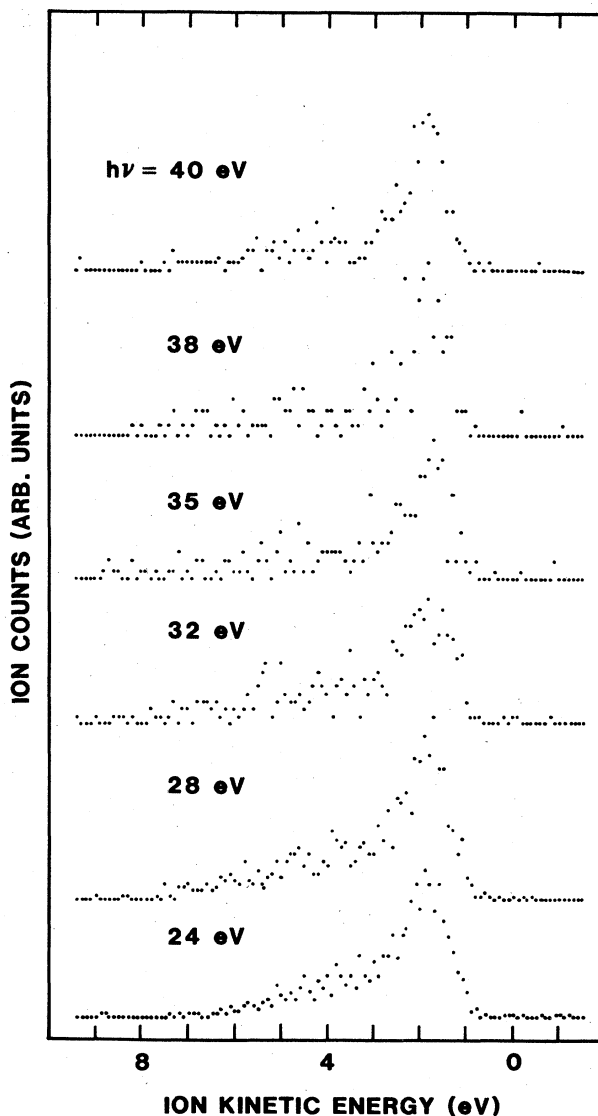


FIG. 3. Ion-kinetic-energy distributions for photon energies between 24 and 40 eV. The curves have all been normalized to the same intensity.

ESD of H<sup>+</sup> from a hydrogenated Si surface; a peak near 2-eV kinetic energy asymmetrically broadened to higher kinetic energies. The data reported here are also comparable to that reported for H<sup>+</sup> and H<sup>\*</sup> produced by electron impact of gas-phase methane,<sup>6-8</sup> except that in the latter case the maximum in the IEDC was 2.5 eV. Above  $\hbar\omega = 30$  eV, signal-to-noise ratio in the IEDC's is too poor to determine any significant change in shape as  $\hbar\omega$  is varied. Below these photon energies there is no significant change in shape, suggesting that the desorption process at threshold remains the dominant decay channel up to 30 eV. Since experimental and theoretical studies of the electron-impact-induced dissociation of gas-phase methane indicate that a bare two-hole state should result in the production of H<sup>+</sup> with  $\sim 8$  eV or greater kinetic energy,<sup>7,8,10</sup> then whatever uncertainties are introduced in

comparing the IEDC's of solid- and gas-phase systems, a peak in the IEDC of solid neopentane of 1.9 ( $\pm 0.25$ ) eV, cannot be ascribed to desorption from a bare two-hole state. At least one electron in a bound virtual level must be involved.

#### IV. DISCUSSION

While the predesorptive final state which gives rise to 1.9-eV protons in solid neopentane must include at least one electron to partially screen the two final-state holes, the exact nature of this excitonlike final state cannot be deduced from the current data. It is not unreasonable that the process which gives rise to 1.9-eV protons in condensed neopentane is similar to the process which yields 2.5-eV protons and excited neutrals in gas-phase methane. The 20 ( $\pm 1$ )-eV PSD threshold for the solid corresponds closely to the 22.17 ( $\pm 0.1$ )-eV ESD threshold for non-thermal  $H^+$  observed for gas-phase methane.<sup>6</sup> The work of Sambe *et al.*<sup>17</sup> indicates that ions desorbed from a surface will be retarded by the interaction potential between the positive ion and its induced polarization at the surface. Since the bulk polarization of polyethylene is 1.5 eV (Ref. 13) and the surface polarization might be less, this could account for the 0.6 ( $\pm 0.25$ )-eV difference in the IEDC's of solid neopentane and gas-phase methane. Assuming this correspondence to be the case, the exact nature of the state in gas-phase methane which gives rise to 2.5-eV protons and excited neutrals is unknown. The production of 4-eV protons and excited neutrals from methane has been associated with the direct excitation of the  $(1t_2^{-2}, 3a_1^1)$  state, with a minimum excitation energy of  $\sim 25$  eV.<sup>9</sup> Any two-hole one-electron state giving rise to 2.5-eV particles would presumably have to have the screening electron more tightly bound than the  $3a_1$  level, and this does not appear possible for methane.<sup>18</sup> A similar argument can be made for neopentane,<sup>19</sup> suggesting that the states which are associated with the 1.9-eV kinetic-energy channel in solid neopentane and the 2.5-eV channel in gas-phase methane include two or more electrons in bound virtual levels.

A problem with the above arguments, however, is that if the state excited near threshold in solid neopentane is of the multihole, multielectron variety, one would expect a significant shift of the IEDC maximum to higher kinetic energies once  $\hbar\omega$  becomes greater than the minimum necessary to excite the  $(3t_2^{-2}, 3a_1^1)$  (two-hole-one-electron) state. While the normalized ion yield shows that there are other resonances at  $\hbar\omega > 30$  eV, the maximum in the IEDC remains at 1.9 ( $\pm 0.25$ ) eV up to  $\hbar\omega \sim 45$  eV. This

would be explained if in neopentane the  $(3t_2^{-2}, 3a_1^1)$  state has a much lower excitation probability, even near resonance, than the state which gives rise to the 1.9-eV protons. A definitive answer to this question, however, requires a better signal-to-noise ratio for both the ion yield and IEDC's for  $\hbar\omega \geq 30$  eV.

A final point involves a comparison of the neopentane and  $H^+$ /Si:H data.<sup>16</sup> The Si-H bond length in  $SiH_4$  is 1.48 Å (Ref. 20) and presumably is close to that for an SiH surface. For solid neopentane, the C-H bond length is  $\sim 1.09$  Å.<sup>20</sup> If in both cases  $H^+$  ions were being produced from a bare two-hole state, one would expect that the ratios of the  $H^+$  kinetic energies would be in inverse proportion to the ratios of the bond lengths. That this is not the case is evidence that, in at least one and probably both cases, the final-state hole-hole repulsion is moderated by electron-hole attraction due to at least one screening electron associated with the final-state holes.

#### V. SUMMARY AND CONCLUSIONS

The ion-kinetic-energy distributions and normalized ion yield resulting from the PSD of solid neopentane have been observed for photon-excitation energies between 17 and 45 eV. The normalized ion yield has a threshold at 20 ( $\pm 1$ ) eV and maximum at 24.5 eV, indicating that at these energies the ion ( $> 94\%$   $H^+$ ) desorption process is associated with excitation of the C 2s level. The possible existence of maxima at higher photon energies, indicative of other resonances, cannot be determined due to the small photon flux at energies  $> 30$  eV. Ion-kinetic-energy distribution curves, at all photon energies, display a main peak at 1.9 ( $\pm 0.25$ ) eV. This kinetic energy is too small to correspond to desorption from a bare two-hole state, and indicates the presence of at least one electron in a bound virtual level.

#### ACKNOWLEDGMENTS

The work at Sandia National Laboratories and the University of Wisconsin was supported by the U. S. Department of Energy under Contract No. DE-AC04-76DP00789, by the U. S. Office of Naval Research under Project No. N00014-80-C0908, and by the National Science Foundation under Grant No. DMR-81-00518. The experiments were made possible by the expert assistance of the staff of the University of Wisconsin Synchrotron Radiation Center (supported by the National Science Foundation under Grant No. DMR-80-20164). The authors would also like to thank E. B. Stechel and D. R. Jennison for making known to us their results prior to publication.

\*On leave from Jagellonian University, PL-30-059 Cracow, Poland.

†Permanent address: Department of Physics and Astronomy, Vanderbilt University, Nashville, TN 37235.

<sup>1</sup>R. A. Rosenberg, V. Rehn, A. K. Green, P. R. LaRoe, and C. C. Parks, in *Desorption Induced by Electronic Transitions*,

edited by N. H. Tolk, M. M. Traum, J. C. Tulley, and T. G. Madey (Springer, Berlin, 1983), p.247.

<sup>2</sup>D. Hanson, R. Stockbauer, and T. E. Madey, *J. Chem. Phys.* **77**, 1569 (1982).

<sup>3</sup>R. Stockbauer, E. Bertel, and T. E. Madey, *J. Vac. Sci. Technol.* **A1**, 1162 (1983).

- <sup>4</sup>J. A. Kelber and M. L. Knotek, *Surf. Sci.* **121**, L499 (1982).
- <sup>5</sup>J. A. Kelber and M. L. Knotek, *J. Vac. Sci. Technol.* **A1(2)**, 1149 (1983).
- <sup>6</sup>R. Locht, J. L. Olivier, and J. Momigny, *Chem. Phys.* **43**, 425 (1979).
- <sup>7</sup>M. D. Burrows, S. R. Ryan, W. E. Lamb, Jr., and L. C. McIntyre, Jr., *J. Chem. Phys.* **71**, 4931 (1979).
- <sup>8</sup>T. G. Finn, B. L. Carnahan, W. C. Wells, and E. C. Zipf, *J. Chem. Phys.* **63**, 1596 (1975).
- <sup>9</sup>C. Backx, G. R. Wright, R. R. Tol, and M. J. VanderWiel, *J. Phys. B* **8**, 3007 (1975).
- <sup>10</sup>E. B. Stechel and D. R. Jennison (unpublished).
- <sup>11</sup>M. M. Traum and D. P. Woodruff, *J. Vac. Sci. Technol.* **17**, 1202 (1980).
- <sup>12</sup>J. A. Kelber and M. L. Knotek (unpublished).
- <sup>13</sup>J. J. Pireaux, R. Caudano, S. Svensson, E. Baslier, P.-A. Malmqvist, U. Gelius, and K. Siegbahn, *J. Phys. (Paris)* **38**, 1221 (1977).
- <sup>14</sup>K. Seki, S. Hashimoto, N. Sato, Y. Harada, K. Ishii, H. Inokuchi, and J. Kanbe, *J. Chem. Phys.* **66**, 3644 (1977).
- <sup>15</sup>J. J. Pireaux, R. Caudano, S. Svensson, E. Baslier, P.-A. Malmqvist, U. Gelius, and K. Siegbahn, *J. Phys. (Paris)* **38**, 1213 (1977).
- <sup>16</sup>H. H. Madden, D. R. Jennison, M. M. Traum, G. Margaritondo, and N. G. Stoffel, *Phys. Rev. B* **26**, 896 (1982).
- <sup>17</sup>H. Sambe, M. Yousif, and D. E. Ramaker, *J. Vac. Sci. Technol.* (to be published).
- <sup>18</sup>M. B. Robin, *Higher Excited States of Polyatomic Molecules* (Academic, New York, 1974), Vol. 1.
- <sup>19</sup>K. E. Johnson, K. Kim, D. B. Johnston, and S. Lipsky, *J. Chem. Phys.* **70**, 2189 (1979).
- <sup>20</sup>*Tables of Interatomic Distances and Configurations in Molecules and Ions*, edited by A. D. Mitchell and L. L. Cross (Chemical Society, London, 1958), pp. S10, M186.