Long-Range Ion-Atom Interactions Studied by Field-Dissociation Spectroscopy of Molecular Ions

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A long-range ion-atom potential is for the first time measured directly by electric-field–induced dissociation of selectively laser-excited $O_2{}^+$ ions in a fast beam. The laser excitation spectrum reflects the molecular properties at "normal" internuclear distances of 1–2 Å while the threshold field required to dissociate the excited molecule determines the O^+-O potential in the range 10–20 Å.

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This Letter reports on the first direct determination of an ion-atom interaction potential at distances of 10–20 Å by means of electric-field–induced dissociation of selectively laser-excited molecular ions. Contrary to previous field-dissociation experiments,[1,2] the field-induced dissociation of the selectively excited molecules sets in at a well defined threshold, which is directly related to the long-range ion-atom interaction potential. So far, such potentials have only been available from theoretical calculations[3] despite their importance in low-energy collisions, dissociation processes, and "long-range molecules."[4]

Field-induced dissociation of a molecular ion is analogous to the detachment of electrons from Rydberg atoms or negative ions in weakly bound states such as the recently discovered dipole bound states.[5] The analogy implies that dissociation induced by fields on the order of 100 kV/cm can only occur for weakly bound molecules with a large vibrational amplitude. According to the Franck-Condon principle, such long-range states are difficult to prepare by direct excitation of molecules at normal internuclear distances. However, they can be prepared by a mechanism closely related to predissociation: excitation to a normal molecular state at 1–2 Å which through a potential-curve crossing couples to a long-range state.

For the demonstration of field dissociation of selectively excited molecules we chose the ion $O_2{}^+$, which is well known from photofragment spectroscopy.[6–8] The $O_2{}^+$ ions are laser excited from the metastable state $a\,^4\Pi_u$ to selected levels in the vibrational state $v=4$ of $b\,^4\Sigma_g^-$ and $v=1$ of $f\,^4\Pi_g$. These levels couple to the $d\,^4\Sigma_g^+$ state through the curve crossings near 1.6 Å, as illustrated in Fig. 1. The d state correlates to the lowest dissociation limit, $O^+(^4S°)+O(^3P_2)$, and supports a number of weakly bound states with large vibrational amplitudes immediately below this limit. We have previously observed one of these long-range levels of the d state by optical-optical double-resonance photofragment spectroscopy.[8] Normally, the transitions to the d state cannot be observed because of a very small transition moment, but an almost exact accidental degeneracy with the rotational level $N=7$ in the b state perturbs the levels and turns the state into a 50-50 mixture of b and d which can readily be excited from the $a\,^4\Pi_u$ state.

The experimental setup for field-dissociation spec-

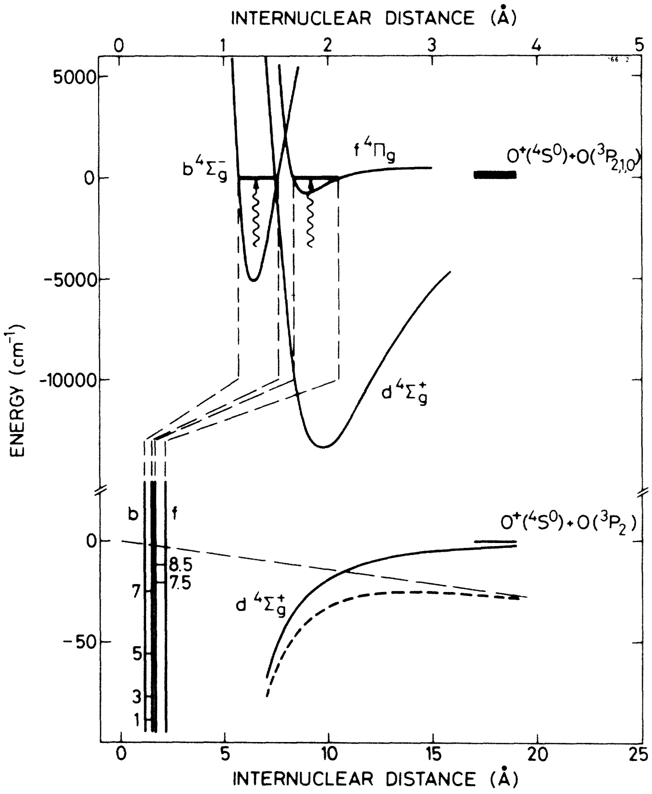

FIG. 1. Potential curves of the three upper levels involved in the field-dissociation spectroscopy of $O_2{}^+$. The upper half of the figure indicates the potential curves at short range. The lower half indicates the same potential curves on an expanded energy scale and a contracted distance scale. The dashed curves indicate the potential and the asymptote for the O-O^+ system with the internuclear axis parallel to an external electric field equal to the threshold field for dissociation of the rotational level $N=7$ ion in the $b\,^4\Sigma_g^+$ $(v=4)$ state.

troscopy is shown in Fig. 2. The $O_2{}^+$ ions are formed in a radio-frequency discharge in oxygen gas. After acceleration to 120 keV and mass selection, the molecular ions enter a 2-m-long field-free drift region where they interact with the beam from a single-mode ring dye laser. Then the ions enter a short region with a high electric field which causes dissociation of those ions that were laser excited to levels a few millielectronvolts below the dissociation limit. The resulting O^+ fragments are electrostatically deflected onto the first dynode of a fast electron multiplier. In order to suppress background from collision-induced dissociation, we use lock-in detection referenced to a mechanical chopper that modulates the intensity of the laser beam.

The field-dissociation unit (strongly oversized in Fig. 2) consists of two polished stainless-steel electrodes 0.66 mm apart. Each electrode has a 0.3-mm-diam hole in the center through which the ion beam enters and exits from the high-field region. An electrostatic relaxation calculation shows that the holes have a marked effect on the electric field near the electrodes while the field in the middle of the gap is fairly homogeneous and is reduced by only 2.5% relative to what it would be in the absence of the holes. The field in the middle of the gap is the highest field experienced by the ions. Fields up to 220 kV/cm were achieved. The strong electric field causes a severe defocusing of the fragment ion beam. This defocusing is reduced by use of a high beam energy and is, furthermore, compensated for by the large sensitive area of the detector. The transit time through the high-field region between the electrodes is 0.8 ns. This is a long time compared to the vibration of the molecule but it is comparable to the predissociation lifetime of the levels in the b state immediately above the dissociation limit.

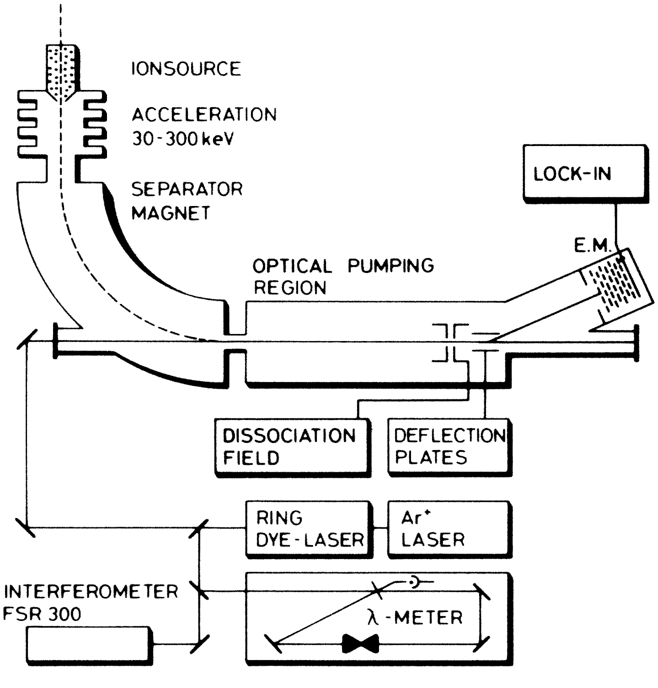

FIG. 2. Experimental setup for field-dissociation spectroscopy.

In the present study we have observed field dissociation of the rotational levels $N = 1$, 3, 5, and 7 in the $b\,^4\Sigma_g^-$ ($v = 4$) state and $J_\Omega = 7.5_{1/2}$ and $8.5_{1/2}$ in the $f\,^4\Pi_g$ state. The excited levels lie 12–90 cm^{-1} (1.5–11 meV) below the lowest dissociation limit, $O^+(^4S^\circ) + O(^3P_2)$. The spectral resolution is 80 MHz (0.003 cm^{-1}), limited by the velocity spread in the fast beam. For comparison, the b-state levels immediately above the dissociation limit are homogeneously broadened to 180–500 MHz because of predissociation by the $d\,\Sigma_g^+$ state.

The high spectral resolution allows the observation of the four individual fine-structure components of each rotational level and of perturbations such as those in the $N = 7$ rotational level that we already mentioned. The present spectra confirm our previous results from optical-optical double-resonance spectroscopy[8] and provide further information for two reasons: The higher sensitivity of the field-dissociation detection scheme allows the observation of weak lines from the perturbing state, and we can now study levels with $J < 5.5$ in $N = 1$, 3, and 5 which could not be observed by optical-optical double resonance because of selection rules. The field-dissociation spectra reveal "new" perturbations in the rotational levels $N = 3$ and $N = 5$.

Such perturbations, due to near degeneracies, are very likely to occur immediately below the dissociation limit because of the high density of vibrational levels in those electronic states that correlate to the limit. They result from the same interaction that gives rise to predissociation above the dissociation limit. The coupling to a long-range state like the d-state level that perturbs $N = 7$ in the b state may be considered the first step towards dissociation of the molecular ion. The dissociation then takes place when the long-range potential is modified by an external field of sufficient strength.

When the laser frequency is resonant with a transition to a level immediately below the dissociation limit and the electric field is increased from zero, field dissociation sets in at a well defined threshold. The threshold occurs at higher fields for more strongly bound levels, as illustrated in Fig. 3 for $N = 1$, 3, 5, and 7 of the b state. This behavior will make the threshold field very valuable in the assignment of the transitions in future applications of field-dissociation spectroscopy to less well known molecular ions. For

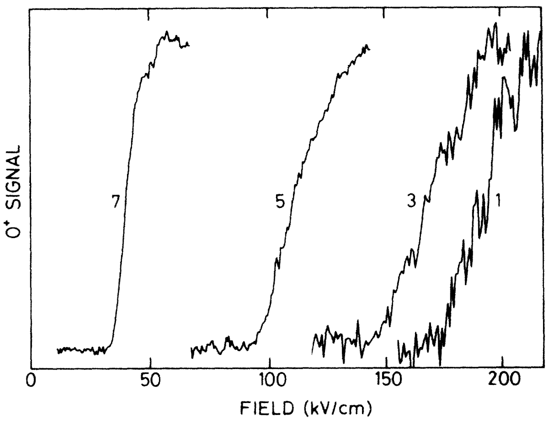

FIG. 3. Laser-induced O$^+$ signal as a function of the electric field for transitions to four different rotational levels, $N = 1, 3, 5$, and 7, in the $b\,^4\Sigma_g^+$ ($v = 4$) state. The four signals have been normalized to the same height at high field.

$O_2{}^+$, however, it is more interesting that the threshold field provides an experimental determination of the long-range potential between O$^+$ and O in their electronic and spin-orbit fine-structure ground states.

Normally, a homonuclear molecular ion like $O_2{}^+$ is considered to have a symmetric charge distribution. This symmetry must be broken in the field-dissociation process—otherwise, the external field would just accelerate the molecular ion as a whole. Therefore, field dissociation must take place at internuclear distances so large that the exchange of electrons between the two atoms is slow compared to the vibrational frequency. This implies that the molecule can be described in terms of an atom and an atomic ion which are bound only by "electrostatic" forces originating from the interaction of the charge of the ion with the quadrupole moment and the induced dipole moment of the neutral atom.[3] We note that the electric field from the ion at the atom is 2 orders of magnitude larger than the external field so that the polarization of the atom by the external field may be neglected.

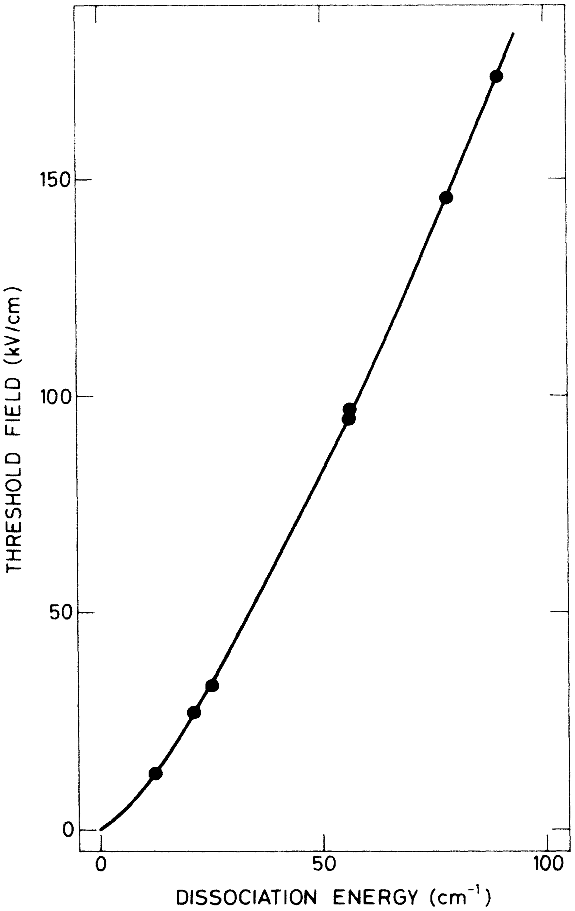

FIG. 4. Field-dissociation threshold as a function of the dissociation energy of the upper level. The curve is calculated from Eqs. (2) and (3) for the theoretical long-range potential of Gentry and Giese (Ref. 3). There is only one free parameter: the energy of the dissociation limit.

The dissociation will preferentially occur with the molecular axis parallel to the external field. In the center-of-mass frame, the external field, E, then simply adds an extra term $-eER/2$ to the potential of the molecular ion, $V(R)$, so that the total potential becomes

$$U(R) = V(R) - eER/2, \tag{1}$$

where R is the internuclear distance. This potential has been included in Fig. 1 with a value of E corresponding to the threshold field for dissociation of the $N = 7$ level in the b state. Whereas tunneling may be important in the field dissociation of $H_2{}^+$,[9] it is negligible for $O_2{}^+$ because of the heavier mass. Accordingly, the maximum of $U(R)$ at the threshold field, E_0, equals the dissociation energy of the excited state:

$$D = U(R_0) = V(R_0) - eE_0R_0/2, \tag{2}$$

where R_0 is the internuclear distance at the maximum of $U(R)$. Generally, R_0 is larger than the internuclear distance at the outer turning point for the classical vibration in the zero-field potential, $V(R)$. At the maximum of $U(R)$, we have from Eq. (2)

$$U'(R_0) = 0 = V'(R_0) - eE_0/2. \tag{3}$$

The values of D can be determined to spectroscopic precision (0.002 cm^{-1}) except for a common constant: the energy of the dissociation limit. The threshold field, E_0, taken as the electric field in the middle of the gap between the electrodes at the onset of field-induced dissociation, can be determined to a precision of $\sim 2\%$. For a set of corresponding values of D and E_0, Eq. (3) can be integrated by use of Eq. (2) to yield a determination of the zero-field ion-atom potential, $V(R)$. Alternatively, corresponding values of D and E_0 can be calculated from Eqs. (2) and (3) for a given theoretical potential, $V(R)$, which allows a direct comparison with the experimental data.

In Fig. 4, such a comparison is made for the theoretical ion-atom potential, $V(R)$, derived by Gentry and Giese[3] from the Hartree-Fock values for the quadrupole moment and polarizability of the oxygen atom. The agreement is quite remarkable and indicates how well long-range molecules can be described in terms of the properties of the individual atoms.[3,4] The values of R_0 range from 9.9 Å for $N=1$ in $b\,^4\Sigma_g^+$ $(v=4)$ to 17.8 Å for $J_\Omega = 8.5_{1/2}$ in $f\,^4\Pi_g$. The only free parameter in the plot in Fig. 4 is the energy of the dissociation limit. Our best value for the limit is 14.7 ± 0.3 cm^{-1} below the lowest predissociating level in the b $(v=4)$ state: $N=9$. This is in perfect agreement with the 14.2 ± 1.7 cm^{-1} obtained by Pernot *et al.*[10] from the kinetic energy released in the predissociation. It should be noted that our uncertainty does not include possible systematic errors due to failure of the model for the long-range potential.

Already in its present form field-dissociation spectroscopy gives a unique picture of the molecular dissociation process from the interactions at the potential-curve crossing at short range to the ion-atom interaction in the almost dissociated long-range molecule. The technique will probably be useful in the study of potential-curve crossings at long range between different electronic states that correlate to the same limit, and for lighter molecular systems it will allow studies of tunneling through a potential barrier with the height and width completely controlled via the external electric field.

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