Electron Detachment via Charge Transfer to Shape Resonances in H^--O_2 and H^--NO Collisions

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Spectra of low-energy electrons ejected in the collisions of 2.5-keV H^- with O_2 and NO have been studied. Charge transfer to the shape resonances, $O_2^-(^2\Pi_g, v'' \geq 4)$ and $NO^-(^3\Sigma^-, v'' \geq 1)$, was found to be the predominant route for the electron detachment. It was also found that Wigner's threshold law was sensitively reflected in the vibrational structures of the spectra.

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In the collisions of negative ions with molecules, electron detachment via charge transfer to shape resonances (CTSR) has attracted recent attention as one of the possible detachment mechanisms. Risley has observed regularly structured spectra of electrons autodetached from the N_2^- $^2\Pi_g$ resonance formed by H^--N_2 collisions.[1] Cheung and Datz[2] and Annis *et al.*[3] have suggested a role of CTSR in Cl^--H_2 and Cl^--N_2 collisions from their differential time-of-flight (TOF) studies of the scattered neutrals. More recently, Tuan and Esaulov[4] have performed TOF studies of the relative role of the CTSR in comparison to the direct detachment (DD) mechanism which is considered to give rise to a continuous spectrum of electrons in a low-energy range (mostly lower than 1 eV). They found that the CTSR was more important than the DD in H^--N_2 and H^--CO collisions. Montmagnon *et al.*[5] have investigated the energy spectra of electrons detached in H^--N_2 and H^--H_2 collisions and have shown that the charge transfer to the N_2^- $^2\Pi_g$ resonance becomes more important as the collision energy increases from 10 to 750 eV.

We report here some results of a study of the electron detachment in the collisions of 2.5-keV H^- ions with O_2 and NO molecules. Electron-impact studies[6-8] have shown that the negative-ion shape resonances of O_2^- $(X\,^2\Pi_g, v'' \geq 4)$ and NO^--$(X\,^3\Sigma^-, v'' \geq 1)$ have lifetimes much longer than those of the N_2^- $^2\Pi_g$ and the CO^- $^2\Pi$ resonances. The O_2^- and the NO^- shape resonances are located very close to the ground neutral states (low resonance energies) and classified as the "compound-state limit"[9] since their autodetachment widths are much smaller than their vibrational spacings. We have measured spectra of electrons detached in the energy range from 0 to 1 eV aiming to see a role of charge transfer to these resonances in the compound-state limit relative to the DD mechanism.

The experimental procedures were briefly as follows: The H^- ions, extracted from a duoplasmatron discharge source, were deflected through 90° in an electrostatic deflector, mass selected in a Wien filter, and accelerated to a final impact energy of 2.5 keV before intersecting an effusive beam of the target molecular gases. The energy analysis of detached electrons was made by means of a 180° hemispherical electrostatic deflector with a mean radius of 35 mm. Electrons ejected at an emission angle of 90° with respect to the incident ion-beam direction were accelerated through a set of cylinder lenses up to an energy of 9 eV before entering the hemispheres which were operated in the constant deflection voltage mode. Energy spectra of electrons detached with their initial energies ranging from 0 to 1 eV were obtained by sweeping the accelerating voltage between 9 and 8 eV. The energy resolution was about 80 meV full width at half maximum (FWHM).

Figure 1(a) shows an energy spectrum of the electrons from H^--O_2 collisions. The spectrum is composed of structures wholly attributable to the autodetachment from the O_2^- $^2\Pi_g$ resonance, demonstrating that CTRS is the predominant route for the detachment of the low-energy electrons. The energy separations between the neighboring two maxima in the spectrum coincide with the vibrational spacings of the O_2^- shape resonance.[7] A significant feature of the spectrum is that all the peaks correspond to transitions only to the ground vibrational level of the neutral state, viz.,

$$O_2^-(^2\Pi_g, v'' \geq 4) \rightarrow O_2(X\,^3\Sigma_g^-, v'=0) + e. \qquad (1)$$

Quite the same characteristic features were found for the electrons detached in H^--NO collisions. A spectrum of electrons from the 2.5-keV H^--NO system is shown in Fig. 2(a). The

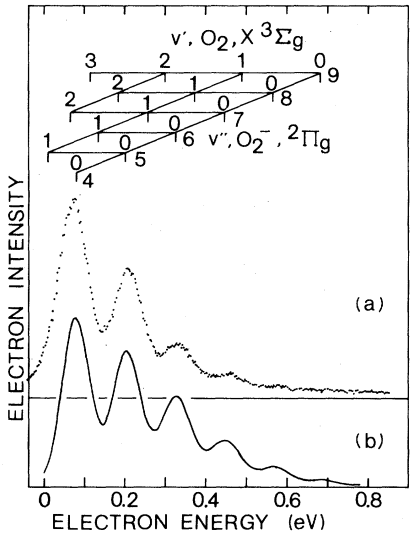

FIG. 1. (a) Energy spectrum of electrons detached in 2.5-keV H^--O_2 collisions observed at 90°. (b) Calculated energy spectrum of electrons autodetached from the O_2^- $^2\Pi_g$ resonance.

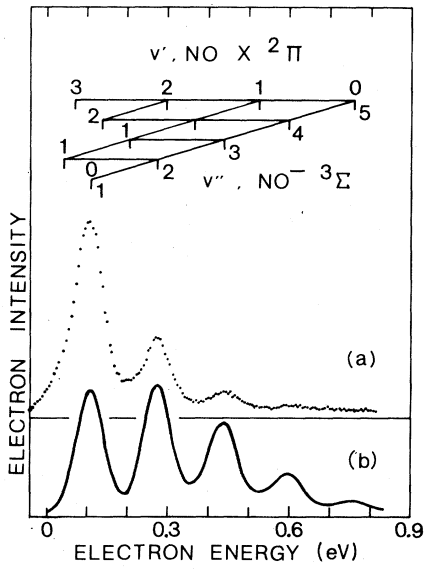

FIG. 2. (a) Energy spectrum of electrons detached in 2.5-keV H^--NO collisions observed at 90°. (b) Calculated energy spectrum of electrons autodetached from the NO^- $^3\Sigma$ resonance.

spectrum is composed of vibrational structures due to the autodetachment from the NO^- ($X\,^3\Sigma$, $v'' \geq 1$) resonances. In this case again, all the peaks in the spectrum correspond to transitions to the ground level $v' = 0$ of the neutral state $NO(X\,^2\Pi)$.

The spectra in Figs. 1(a) and 2(a) are not corrected for the transmission function of the lens system through which electrons are accelerated and focused into the hemispheres. The transmission function was checked by observing continuum spectra of electrons produced by electron impact on He atoms at collision energies slightly above the He ionization threshold under various lens conditions. The spectra in Figs. 1(a) and 2(a) were obtained under the lens conditions adjusted so as to result in an optimum transmission on the lowest-energy peak of the spectra. Under these conditions, the relative transmission function was estimated to be rapidly decreasing from 100% to 60% as the electron energy increased from 0 to 70 meV, and then slowly decreasing from 60% to 45% as the electron energy increased from 70 to 900 meV.

We have calculated a spectrum which can be reconciled with the observed one on the assumption that the energy spectrum of electrons which are autodetached from a resonant level v'' and leave the neutral state in a level v' would be, for a resonance in the compound-state limit, given by

$$S_{v''v'}(E) = \frac{C}{2\pi} \frac{n_{v''}\,\Gamma(E_{v''v'})\,|\langle \chi_{v''} | \zeta_{v'} \rangle|^2}{(E - E_{v''v'})^2 + (\gamma_{v''}/2)^2}. \quad (2)$$

Here C is a constant. $n_{v''}$ is the population in the level v''. $\Gamma(E)$ is the width function of the resonant state. $E_{v''v'}$ is the energy difference between the resonant level v'' and the neutral level v'. χ and ζ are vibrational wave functions of the resonant and the neutral states, respectively. $\gamma_{v''}$ is the total decay width of the resonant level v'', viz.,

$$\gamma_{v''} = \sum_{v'} \Gamma(E_{v''v'})\,|\langle \chi_{v''} | \zeta_{v'} \rangle|^2.$$

For a comparison to observation, the spectrum in Eq. (2) should be convoluted by a resolution function $T_{\delta E}(E)$ of the apparatus with an energy resolution δE,

$$I(E) = \sum_{v'',v'} \int T_{\delta E}(E - E')\, S_{v''v'}(E')\, dE'. \quad (3)$$

The present resolution δE, which is about 80 meV FWHM, is much larger than the total width $\gamma_{v''}$ of the level v'' in the O_2^- and the NO^- shape resonances.[10,11] Equation (3) may thus be approximated as

$$I(E) \simeq \sum_{v'',v'} T_{\delta E}(E - E_{v''v'}) \int S(E')\, dE' = C \sum_{v'',v'} T_{\delta E}(E - E_{v''v'})\, n_{v''} R(v'', v'), \quad (4)$$

where $R(v'',v')$ is the branching ratio of the autodetachment decaying from the level v'',

$$R(v'',v') = \Gamma(E_{v'',v'})|\langle\chi_{v''}|\zeta_{v'}\rangle|^2/\gamma_{v''}. \quad (5)$$

Risley[1] has proposed models in approaching the energy spectra of electrons detached from the N_2^- $^2\Pi_g$ resonance. The decay width $\gamma_{v''}$ of the N_2^- resonance, which is about 0.2 eV,[1] is much larger than those of the O_2^- and the NO^- resonances. If the resolution width δE is set to be much smaller than the decay width $\gamma_{v''}$, the integration in Eq. (3) may be evaluated by putting the line-shape function $S_{v'',v'}(E)$ outside of the integration, and the resulting expression is almost similar to one of the models proposed by Risley. However, as has been stated by Risley,[1] the N_2^- resonance has special problems arising from the fact that resonance lifetime is on the order of one vibrational period. This invokes further considerations in treating the Franck-Condon factors and the resonance energies. The present approach should thus be applied to resonances in the compound-state limit such as the O_2^- and the NO^- shape resonances.

From Wigner's threshold law,[12] a strong energy dependence of $\Gamma(E)$ is expected to occur for low-energy electrons freed from the resonances. Semiempirically parametrized forms based on Wigner's law have been presented for the width function of the resonances[10,11] as

$$\Gamma(E) = C_1 E^{5/2} \text{ for the } O_2^- \ ^2\Pi_g, \quad (6)$$

and

$$\Gamma(E) = C_2 E^{3/2}(1 + 2.5E) \text{ for the } NO^- \ ^3\Sigma^-. \quad (7)$$

The parameters C_1 and C_2 cancel out in the branching ratios. Tables I and II list the branching ratios calculated by Eqs. (5)–(7). The molecular spectroscopic constants used for calculating the Franck-Condon factors were taken from Refs. 10 and 11. The branching ratios in the tables indicate that the decay from lower vibrational levels v'' leads most preferentially to the ground level $v' = 0$. This is a consequence of the strong energy dependence of $\Gamma(E)$ near the threshold. Transitions from higher v'' levels, however, prefer to go to higher final levels $v' > 0$ since the Franck-Condon factors are quite small between the higher v'' levels and the $v' = 0$ level. The decay from the higher v'' level does not significantly contribute to the observed spectrum, indicating that the population $n_{v''}$ resulting from the charge transfer process is quite small for the higher v'' levels. We calculated energy spectra with Eqs. (4) and (5), assuming a Gaussian form with a width of 80 meV FWHM for the resolution function, and assuming that the populations $n_{v''}$ are given by the Franck-Condon factors $|\langle\chi_{v''}|\zeta_0\rangle|^2$. The calculated spectra are shown in Figs. 1(b) and 2(b). The calculation for the O_2^- resonance agrees farily well with the observation. For the NO^- resonance, a discrepancy is seen in the relative peak height between the observed and the calculated spectra. The discrepancy suggests that charge transfer between H^- and NO might result in more preferential populations in the lower v'' levels of the NO^- resonance than the populations expected from the Franck-Condon factors.

In conclusion, the present study indicates that charge transfer to the O_2^- and the NO^- shape resonances is the predominant mechanism of low-energy electron detachment in the collisions of 2.5-keV H^- ions with O_2 and NO molecules, and that the vibrationally selective structures in the spectra of electrons autodetached from the O_2^- and the NO^- shape resonances can be understood from Wigner's threshold law. The Franck-Condon population seems to be nearly valid for the formation of the resonant vibrational states in the charge-transferring H^--O_2 collisions, but does not seem to be valid in the H^--NO collisions.

Just prior to the submission of this Letter, we were informed that quite the same characteristic

TABLE I. Calculated branching ratios of the transition $O_2^-(^2\Pi_g, v'') \rightarrow O_2(^3\Sigma_g, v') + e$.

v' \ v''	4	5	6	7	8	9
0	1	0.9998	0.9077	0.6862	0.4699	0.2967
1		0.0002	0.0923	0.3135	0.5026	0.5679
2				0.0003	0.0275	0.1352
3						0.0002

TABLE II. Calculated branching ratios of the transition $NO^-(^3\Sigma, v'') \rightarrow NO(^2\Pi, v') + e$.

v' \ v''	1	2	3	4	5	6
0	1	0.9995	0.9394	0.6734	0.4027	0.2042
1		0.0005	0.0656	0.3230	0.5643	0.5887
2				0.0036	0.0258	0.2027
3					0.0072	0.0044

features had been observed with a somewhat higher resolution by Itoh, Hege, and Linder[13] on the energy spectrum of electrons detached in the $H^- - O_2$ system at much lower collision energies.

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