

## Wave-function overlap effects in low-energy collisional excitation of $O_2$ by $H_2^+$ , $N_2^+$ , $O_2^+$ , and $CO_2^+$ projectiles

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Excitation of molecular oxygen has been studied in 1.8-keV collisions with projectile ions  $H_2^+$ ,  $N_2^+$ ,  $O_2^+$ , and  $CO_2^+$  by means of energy-loss spectrometry. The dependence of the excitation cross section upon the quantal description of projectile ions is probed. The excitation cross section is largest in the case of collisions with  $H_2^+$  ions, in conformity with computed overlaps of the highest occupied molecular orbitals of the colliding systems.

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Target excitation in low-energy collisions between molecular ions and neutral molecules has, in recent experimental studies, started yielding new information on wave-function overlap effects [1]. Excitation of simple molecules like  $H_2$ ,  $N_2$ ,  $CO$ ,  $NH_3$ ,  $CH_4$ , and  $CCl_4$  has been induced in collisions with molecular projectiles such as  $H_2^+$ ,  $N_2^+$ ,  $CO^+$ ,  $O_2^+$ ,  $CS_2^+$ , and  $CO_2^+$  and energy-loss spectra have been measured that reveal transitions to optically allowed and dipole-forbidden states of the target molecules, as well as to ionic states. Relative oscillator strengths for transitions to individual states have been obtained in such measurements [2]. Moreover, it has been found that in all collisional situations where the projectile ion possessed  $\Sigma$  symmetry and the ground electronic state of the target molecule was also a  $\Sigma$  state, collisional excitation cross sections were large. When the projectile ions possessed  $\Pi$  symmetry, the corresponding excitation cross sections became at least an order of magnitude smaller. These results have been interpreted in terms of wave-function overlap effects: in the case of " $\Sigma$ - $\Sigma$  collisions," there is a large overlap of the wave functions of the highest occupied molecular orbitals (HOMO's) of the collision partners, leading to large cross sections. In contrast, the low cross sections in " $\Pi$ - $\Sigma$  collisions" reflect the small overlap integrals between the projectile and target HOMO's. Calculated overlap integrals have been found to be in good accord with the measured cross section ratios [1].

In order to further explore such wave-function overlap effects, we have extended our high-resolution translational energy spectrometry (TES) studies to collisional excitation of the oxygen molecule.  $O_2$  is a particularly interesting target for wave-function overlap studies because although its ground state has  $\Sigma$  symmetry, with zero total orbital angular momentum, the valence electrons occupy a pair of degenerate antibonding  $\pi^*$  orbitals. Intuitively, it may, therefore, be expected that the overlap of the projectile-target HOMO's would be larger with projectiles having  $\pi^*$  HOMO's and smaller with ions having bonding  $\sigma$  orbitals occupied in the HOMO. Consequently, it might be expected that the excitation cross section for  $O_2$  might be larger with molecular projectiles  $O_2^+$  and  $CO_2^+$  compared to that with  $H_2^+$  and  $N_2^+$

projectiles. However, the contrary is found to prevail: we find in these measurements that the excitation cross section is largest when  $H_2^+$  projectiles are used. Peaks due to target excitation are weakly observable in collisions with  $N_2^+$  projectiles. But the energy-loss spectra obtained with  $O_2^+$  and  $CO_2^+$  projectiles showed no excitation peaks.

Our measurements were performed on a high-resolution ion translational energy spectrometer that has been described in detail elsewhere [3]. In brief, positive ions are produced in a low-pressure, electron-impact ion source by 70–100-eV electrons; these ions are extracted and accelerated by an electrostatic potential of 1.8 kV, and are collimated into a thin pencil beam by a three-element, cylindrical electrostatic lens system. Mass analysis of the ion beam is accomplished by a crossed electric and magnetic field sector (Wien filter). The mass-analyzed ions are then energy monochromated by a large, 55-cm radius,  $90^\circ$  cylindrical, electrostatic sector. The monoenergetic ions are then made to collide with the  $O_2$  target, under single collision conditions, in a cell maintained at a pressure of approximately  $5 \times 10^{-4}$  Torr. Forward-scattered projectile ions are energy analyzed by a second, identical  $90^\circ$  cylindrical, electrostatic sector analyzer and are detected by a channel electron multiplier operated in the pulse counting mode, using conventional pulse counting electronics coupled to a computerized data acquisition system.

With the large sectors our instrument is capable of energy resolving powers in excess of  $2 \times 10^4$ . The angular resolution of the apparatus is approximately  $0.1^\circ$ , so that the energy-loss spectra described here yields information on differential excitation cross sections at a scattering angle of  $(0 \pm 0.1)^\circ$ . Use of a low-pressure, electron-impact ion source implies that ions will be extracted in a mixture of ground and metastable states, with a possibility that some of the latter components may survive until the ion beam reaches the collision cell. However, by choosing appropriate experimental conditions (mainly the gas pressure within the ion source and the electron energy), the contribution due to long-lived excited electronic states can be eliminated; participation of any remaining projectile excited species in the excitation process results in

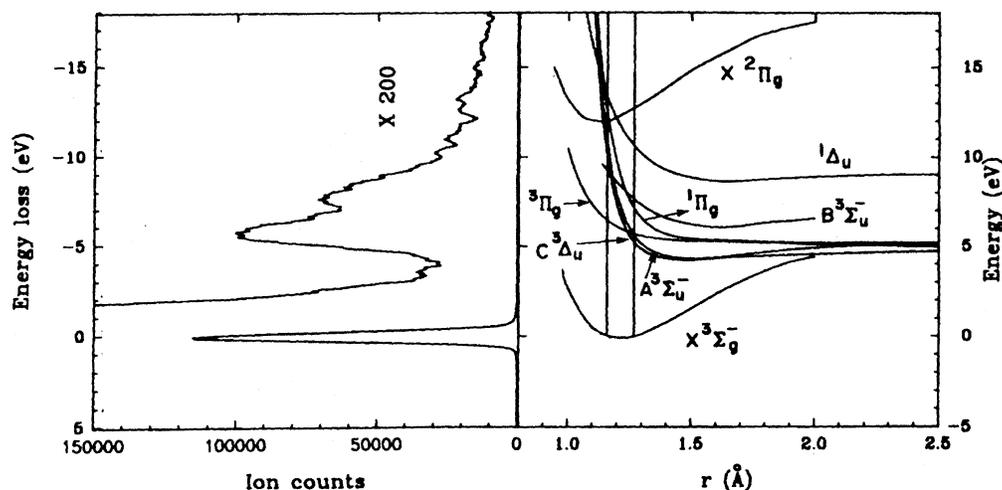


FIG. 1. Energy-loss spectrum of forward-scattered  $\text{H}_2^+$  ions at 1.8-keV incident energy colliding with  $\text{O}_2$  molecules (left panel) and the potential energy functions of some low-lying electronic states of  $\text{O}_2$  and  $\text{O}_2^+$  accessed during collisional excitation (right panel). The vertical lines in the right panel indicate the Franck-Condon region for transitions from the zeroth vibrational level of the ground electronic state,  $^3\Sigma_g^-$ , of  $\text{O}_2$ .

peaks with an energy loss that is distinguishable from the energy-loss values due to the participation of ground state projectile ions. In the present study such processes were not of importance.

Figure 1 shows a typical energy-loss spectrum obtained when  $\text{H}_2^+$  ions in the ground electronic state,  $^2\Sigma_g^+$ , collide with  $\text{O}_2$  at 1.8-keV kinetic energy, under single collision conditions and zero degree scattering angle. The ions transmitted at  $\Delta E \neq 0$  participate in inelastic collisions, wherein part of the projectile ion kinetic energy is converted into potential energy of the colliding

species. Under our kinematic conditions of large impact-parameter collisions with negligible momentum transfer (ensured by the forward-scattering geometry), the energy-loss envelope obtained in Fig. 1 can be attributed entirely to excitation of  $\text{O}_2$  from the ground electronic state ( $X^3\Sigma_g^-$ ) to various excited states indicated by the potential energy curve diagram in Fig. 1. Specifically, the overall shape of the energy-loss envelope is due to excitation of the electron from the outermost  $\pi^*$  orbital of  $\text{O}_2$  to a whole range of close-lying triplet as well as singlet states. Excitation to  $\text{O}_2^+$  ionic states ( $X^2\Pi_g$ , and

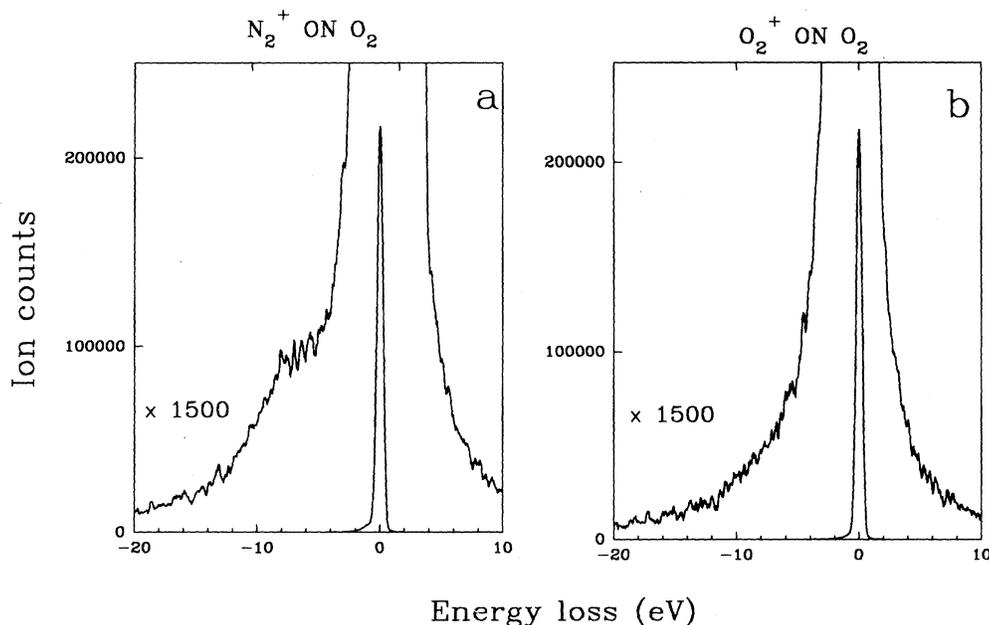


FIG. 2. (a) Energy-loss spectrum of  $\text{N}_2^+$  ions colliding with  $\text{O}_2$  molecules and (b) corresponding spectrum for  $\text{O}_2^+$  projectiles.

TABLE I. Calculated values of the magnitude of the overlap integral ( $I$ ) for different projectile ions colliding with  $O_2$  in the orientation depicted in Fig. 3 using  $H_2^+$  as an example. The calculations are carried out for fixed values of impact parameter  $b$  while  $c$ , the horizontal distance between the center of masses, is varied. The bottom row shows the square of the overlap integrals summed over a range of impact parameters.  $P^* = (H_2^+, N_2^+, O_2^+, CO_2^+)$ .

$b$ (Å)	$c$ (Å)	$I(H_2^+-O_2)$	$I(O_2^+-O_2)$	$I(N_2^+-O_2)$	$I(CO_2^+-O_2)$
2	2	0.0305	0.0011	0.0295	0.00007
2	1	0.0322	0.0053	0.0160	0.0137
2	0	0.0	0.0297	0.0	0.0380
3	2	0.0223	0.0013	0.0042	0.0037
3	1	0.0122	0.0043	0.00008	0.0167
3	0	0.0	0.0122	0.0	0.0363
4	2	0.0017	0.0003	0.0	0.0016
4	1	0.0013	0.0009	0.0	0.0045
4	0	0.0	0.0020	0.0	0.0076
$\sum_{b=2}^{b=4} \sum_{c=-2}^{c=2}  I(P^*-O_2) ^2$		0.0054	0.0023	0.0011	0.0038

beyond) also contribute at larger values of energy loss. Due to the large density of close-lying states the overall energy-loss spectrum yields a large unresolved envelope, even when measurements are made at an energy resolution of better than approximately 0.4 eV (full width at half maximum of the elastic scattering peak obtained at  $\Delta E = 0$ ).

Figure 2 shows spectra obtained when  $N_2^+$  and  $O_2^+$  projectiles were used. The former projectile possesses an overall  $\Sigma$  symmetry, and its HOMO is a bonding  $\sigma$  orbital. The latter projectile possesses a  $\pi^*$  HOMO. Many spectra were taken and they indicated that whereas very weak energy-loss features could be observed in the case of  $N_2^+$  projectiles (observed usually as a shoulder in the energy-loss region beyond 4 eV), absolutely *no* such features were observed when either  $O_2^+$  or  $CO_2^+$  projectiles were used.

In order to gain some further insight, we have calculated the overlap integrals of the HOMO's of the different

collision systems. The wave functions were obtained from linear combinations of the atomic wave functions, using a 6-311G\* Gaussian basis set. The coefficients for the linear combinations were determined by the self-consistent field Hartree-Fock procedure. Table I shows the magnitude of the overlap integrals ( $I$ ) obtained for different impact parameters  $b$  and  $c$ , the distances between the center of masses of the  $O_2$  target and each of the projectiles as defined in Fig. 3. The bottom row in the table shows the square of the overlap integrals summed over a range of impact parameters; the chosen values of impact parameter are in conformity with the high angular resolution of our apparatus, which discriminates strongly in favor of inelastic processes resulting from long-range interactions. It is found at  $c = 0$ , where the colliding systems are exactly one over the other, the intuitively expected symmetry rules are perfectly valid and the overlap integrals of  $O_2$  with the two  $\Sigma$  projectiles ( $H_2^+$  and  $N_2^+$ ) are zero. However, at nonzero values of  $c$ , the overlap integrals are larger with  $H_2^+$  projectiles than with any other colliding ion. In a collisional excitation process all possible orientations of approach for the interacting molecular systems are possible, and would thus lead to larger excitation cross sections in the case of  $H_2^+$ , as is, indeed, observed. In the case of  $N_2^+$  projectiles, the overlap integrals are significantly smaller; in the other cases of  $\pi^*$ - $\pi^*$  interactions (i.e., with  $O_2^+$  and  $CO_2^+$  projectiles), moderate values of overlap integrals are obtained.

In summary, we have carried out TES experiments on collisional excitation of  $O_2$  molecules whose ground state has  $\Sigma$  symmetry but whose valence electrons occupy a pair of degenerate antibonding  $\pi^*$  orbitals. Contrary to the expectations that the excitation cross section for  $O_2$  might be larger with molecular projectiles possessing  $\Pi$  symmetry ( $O_2^+$ ,  $CO_2^+$ ) compared to those with  $\Sigma$  symmetry ( $H_2^+$ ,  $N_2^+$ ), our energy-loss spectra indicate that the excitation cross section is largest when  $H_2^+$  projectiles are used; much weaker excitation is observed with  $N_2^+$  projectiles and virtually no excitation occurs with

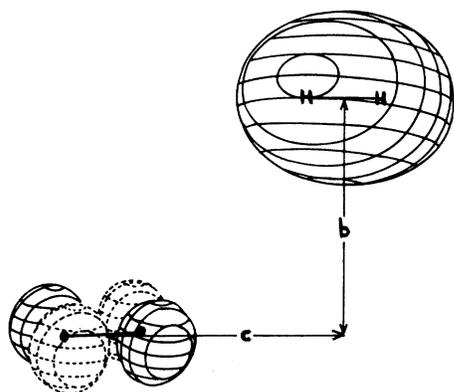


FIG. 3. Plot of the approach of a  $H_2^+$  projectile towards the  $O_2$  target molecule at an impact parameter  $b$ ; the horizontal distance between the center of masses is  $c$ .

$O_2^+$  and  $CO_2^+$  projectiles. Concomitant wave-function overlap calculations have been carried out whose results indicate that  $H_2^+$  projectiles should yield the highest excitation cross sections, whereas only moderate amounts of excitation should be expected with  $O_2^+$  and  $CO_2^+$  projectiles. The accord between experiment and calculations is not as impressive as in earlier studies [1,2]. Nevertheless, it is clear that in order to explore the de-

pendence of collisional excitation cross sections on the quantal properties of the collidants, it is not sufficient to consider the overall symmetry of the colliding partners: consideration of the nature of specific (outermost) molecular orbitals appears to be mandatory if wave-function overlap arguments are to be applicable. The relative sizes of the interacting orbitals might also play a hitherto-unsuspected role in the excitation dynamics.

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