

## Vibrational Progressions and Rydberg Series of $O_2^-$ and $NO^-$

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Resonances for collisions of electrons with  $O_2$  and  $NO$  are studied by measuring the derivative of the current transmitted through  $NO$  and  $O_2$ . In both these gases we find vibrational progressions of compound states. The spacings and Franck-Condon factors for these progressions agree with those of the respective positive ions. Thus it appears that these compound states consist of two Rydberg electrons loosely attached to the ion core.

We have recently reported on the development of an electron transmission experiment which measures structure in the total electron-impact cross section with high sensitivity.<sup>1</sup> We have reported<sup>1</sup> the existence of an isolated, sharp resonance in  $CO$  at  $10.04 \pm 0.03$  eV, and two sharp resonances in  $O_2$  at 8.02 and at  $8.25 \pm 0.03$  eV. The observation in  $CO$  has been confirmed and extended by other authors using different methods of observation.<sup>2</sup>

In this Letter we report the observation of a series of *bands* of resonances in  $NO$ , each *band* consisting of a vibrational progression. In  $O_2$ , we find a single *band* consisting of a progression of ten vibrational states of  $O_2^-$  in the energy range 11–13 eV. Because we can now observe vibrational *progressions* of resonances, rather than isolated structures, we are able to identify these resonances more completely. Thus we can compare the spacings of the vibrational progressions and the relative magnitudes of the structures with the known spacings and Franck-Condon probabilities for transitions to various vibronic states. In this manner we are able to identify the nature and the parentage of the observed resonances. We shall show below that the bands of resonances we observe are associated with Rydberg states of the molecules.

*Theoretical considerations.*—Weiss and Krauss<sup>3,4</sup> have suggested from theoretical considerations that Rydberg excited states (but not valence-excited states) can support a Feshbach (or core-excited) resonance of a molecule. The temporary negative-ion complex then consists of two Rydberg electrons trapped in the field of the ion core and the energy of the resonance lies below the energy of the parent. Since Rydberg electrons are nonbonding, the nuclear constants of the ion core should remain essentially unperturbed by the addition of the two extra electrons. Experimentally one expects to observe about the

same vibrational spacings and Franck-Condon factors for the formation of both the  $O_2^+$  and  $O_2^-$  ions.

In any case, the equilibrium positions of negative ions derived from valence states of molecules lie at large internuclear separations,<sup>5</sup> i.e., far outside the normal Franck-Condon region, and thus are not accessible by electron impact from the ground state.

*Experiments.*—The experiment used for the present study has been recently described. We use a trochoidal monochromator<sup>6</sup> to produce an electron beam with an energy spread of about 25 to 40 meV. This beam, aligned by an axial magnetic field, is transmitted through a gas-filled collision chamber, and the unscattered electrons are collected on an electron collector. The energy of the electrons inside the collision chamber is modulated, and only the modulated component of the transmitted current is measured by using a synchronous detector. The signal we measure is proportional to the derivative with respect to electron energy of the total cross section. The energy scale is calibrated by referring the observed structure to the helium  $1s2s^2$  resonance at 19.3 eV, as described in our previous work.<sup>1</sup>

*Results for  $O_2$ .*—Figure 1 shows an  $X$ - $Y$  plot of the derivative of the transmitted current in the 11–13-eV region. A well-developed progression of ten resonances starts at  $11.78 \pm 0.06$  eV. The vertical lines in the figure point to the zero value of the derivative and identify the energy positions of each level of vibration. The latter are numbered on top of the vertical lines while the spacing between adjacent vibrational levels appears between them. Relative Franck-Condon probabilities can be evaluated from the size of the observed structure. Such a measurement is meaningful since the width of the experimentally observed structure does not depend on the vibrational quantum number.

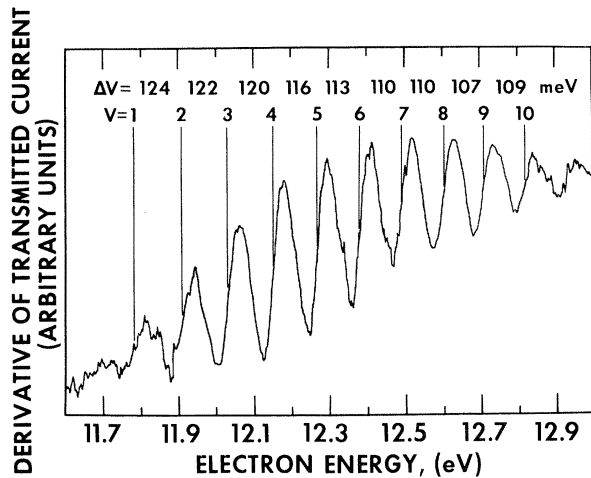


FIG. 1. Derivative of transmitted current versus electron energy in  $O_2$ . We interpret the structure as resulting from a compound state of  $O_2^-$ , with a spacing indicated between the vertical lines. This spacing agrees with the vibrational spacing of the  $O_2^+$  ( $a^4\Pi_u$ ) state, which is the grandparent.

Table I shows a comparison between vibrational spacings and Franck-Condon probabilities of the observed  $O_2^-$  progression and those<sup>7,8</sup> of the  $a^4\Pi_u$  state of  $O_2^+$ . The agreement is seen to be excellent. No such correspondence could be found

when the experimental data are compared with other states of  $O_2^+$ , i.e., the  $X^2\Pi_g$  ground state and the  $A^2\Pi_u$  excited state of  $O_2^+$ . The quantum number of each vibrational level of the  $O_2^-$  state is determined by fitting the Franck-Condon probabilities of the  $O_2^-$  ion to those of the  $O_2^+$  ion. The  $v=0$  level of the  $O_2^-$  progression cannot be observed because its Franck-Condon probability is small.

The resemblance between the nuclear structure of the  $O_2^+$  and  $O_2^-$  ions indicates that the two ions have essentially identical potential energy curves. This is possible if the negative-ion state is composed of two Rydberg electrons trapped by the potential of the  $a^4\Pi_u$  core of  $O_2^+$ . The likely parents of the  $O_2^-$  state could be formed by the addition of a single  $3s\sigma_g$  electron to the  $O_2^+(4\Pi_u)$  core, thus forming  $^3\Pi$  and  $^5\Pi$  Rydberg states. These two Rydberg states lie at 12.50 eV ( $^3\Pi$ ) and 12.24 eV ( $^5\Pi$ ), respectively,<sup>9</sup> and the observed progression lies about 0.6 eV below the ( $^5\Pi$ ) state. Since a value of 0.6 eV is a reasonable value for the electron affinity, we consider this a further confirmation that the  $^3,5\Pi$  states of  $O_2$  are the parents for the observed progression. The addition of an electron of the  $3s\sigma_g$  Rydberg orbital symmetry to the  $^3\Pi$  or the  $^5\Pi$  state of  $O_2$

TABLE I. Comparison of vibrational spacings and Franck-Condon probabilities observed for the progression in  $O_2^-$  found in the present experiment with the appropriate values for  $O_2^+$  ( $a^4\Pi_u$ ).

$v$	Vibrational spacings (meV)		Franck-Condon probabilities	
	$O_2^+$ ( $a^4\Pi_u$ ) $v-l \rightarrow v$ <sup>a</sup>	$O_2^-$ $v-l \rightarrow v$ <sup>b</sup>	$O_2$ ( $X^3\Sigma_g^-, v'=0$ ) $\rightarrow O_2^+$ ( $a^4\Pi_u, v$ ) <sup>c</sup>	$O_2$ ( $X^3\Sigma_g^-, v=0$ ) $\rightarrow O_2^-$ ( $v$ ) <sup>d</sup>
0	...	...	0.076	... <sup>e</sup>
1	126	...	0.278	0.298
2	123	124	0.561	0.447
3	121	122	0.819	0.765
4	118	120	0.986	1.000
5	115	116	1.000	0.980
6	113	113	0.921	0.893
7	110	110	0.783	0.724
8	108	110	0.621	0.596
9	105	107	0.470	0.510
10	103	109	0.341	0.340

<sup>a</sup> Values for the vibrational spacings for the  $O_2^+$  ( $a^4\Pi_u$ ) state from Ref. 7.

<sup>b</sup> The estimated error for the experimental vibrational spacings for  $O_2^-$  is  $\pm 0.003$  eV.

<sup>c</sup> Values for the Franck-Condon probabilities for the  $O_2^+$  ( $a^4\Pi_u$ ) state from Ref. 8.

<sup>d</sup> The estimated error for the experimental Franck-Condon probabilities for  $O_2^-$  is  $\pm 20\%$ .

<sup>e</sup> Not observed.

gives a  ${}^4\Pi$  configuration, which is the suggested designation for the  $O_2^-$  progression. Cross sections for forming quartet compound states are expected to be relatively large in  $O_2$  since this process does not necessitate a spin flip.

It should be noted that the presence of resonances just above the first ionization onset can cause structure in the electron ionization-efficiency curves.<sup>10,11</sup> Two-electron decay of the  ${}^4\Pi$  progression of  $O_2^-$  into the  $X^2\Pi_g$  ground state of  $O_2^+$  becomes energetically possible in the middle of the progression, thus providing a possible new decay channel. However, this decay would involve a three-electron matrix element which is expected to be very small, and thus structure in the  $O_2^+$  ionization cross section would also be small. The observed structure in the ionization cross section of  $O_2$  near threshold<sup>12</sup> is probably due to effects involving a two-electron matrix element.

*Results for NO.*—Figure 2 shows a plot of the derivative of the transmitted current versus electron energy for NO. The locations of four bands of resonances are indicated by the vertical lines. Each band has four vibrational members and starts at 5.04, 5.41, 5.46, and  $6.44 \pm 0.06$  eV, respectively. The vibrational spacings and Franck-Condon probabilities of each band were compared with those of the  $X^1\Sigma^+$  ground state of  $NO^+$ .

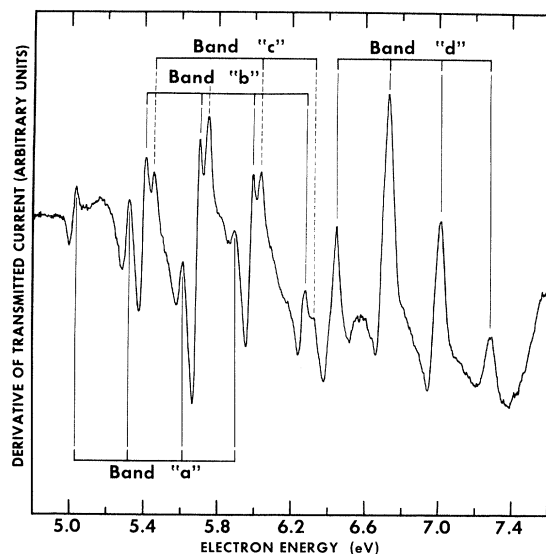


FIG. 2. Derivative of transmitted current versus electron energy in NO. Four bands of a Rydberg series of  $NO^-$  are evident, each band consisting of a vibrational progression. The spacing of the vibrational progression agrees with the vibrational spacing of the  $NO^+$  ( $X^1\Sigma^+$ ) state, which is the grandparent.

Bands *a*, *b*, and *c* have about the same spacings which agree well with those of the positive ion.<sup>13</sup> Band *d* deviates slightly from those values.

Franck-Condon probabilities for bands *a*, *b*, and *d* were obtained from measurements of the relative magnitudes of the resonances. They agree qualitatively with those<sup>8</sup> of the  $X^1\Sigma^+$  state of  $NO^+$ , although bands *a*, *b*, *c* have some degree of overlap.

These comparisons suggest that all four bands are composed of two Rydberg electrons temporarily bound to the same  $X^1\Sigma^+$  core of  $NO^+$ . The parent of band *a* is probably the  $A^2\Sigma^+$  Rydberg state of NO which lies 0.45 eV above it.<sup>9</sup> The *A* state corresponds to an electron in a Rydberg orbital of the symmetry  $3s\sigma$  bound to a  ${}^1\Sigma^+$  positive ion core, and the addition of another  $3s\sigma$  electron to the core gives the  ${}^1\Sigma$  configuration for band *a*. Other configurations can be formed by adding to the grandparent ( $X^1\Sigma^+$  state of  $NO^+$ ) one  $3s\sigma$  electron plus one  $3p\sigma$  or  $3p\pi$  electron. In this case, triplet and singlet compound states can be formed, leading to bands *b*, *c*, and *d*.

*Conclusions.*—We show in this Letter that Feshbach-type (core-excited) resonances in molecules sometimes lead to bands which consist of a vibrational progression of resonances. These can be analyzed and classified by comparing their vibrational spacings and Franck-Condon probabilities with those of the different ion cores. In NO the ion core responsible for the four bands is the  $X^1\Sigma^+$  state of  $NO^+$  whereas in  $O_2$  the 11–13-eV progression results from the  ${}^4\Pi$  state of  $O_2^+$ . One should also expect to observe resonances associated with the  $X^2\Pi$  ion core of  $O_2^+$ . In fact, it was pointed out to us by Krauss<sup>4</sup> that the previously observed resonances<sup>1</sup> at 8.02 and 8.25 eV in  $O_2$  can be interpreted as resulting from the addition of two  $3s\sigma_g$  electrons to the  $X^2\Pi$  ion core of  $O_2^+$ . The spacing between the observed resonances corresponds closely to the spacing of vibrational levels of the ion core<sup>9</sup> of the  $X^2\Pi$  state. The position of the resonances also leads to a reasonable electron affinity if one estimates the energy position of the spectroscopically unobserved parent  ${}^3\Pi$  Rydberg state.

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## Precision Measurement of the Hyperfine Interval of Muonium by a Novel Technique: Ramsey Resonance in Zero Field\*

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A novel method for measuring the hyperfine interval  $\Delta\nu$  of muonium in "zero" magnetic field is described. It consists in applying two successive coherent microwave pulses (lengths  $\tau$ , separation  $T$ ) to muonium, and observing the change in muon polarization at  $t > T + 2\tau$ . By extrapolating two low-pressure runs in Kr we obtain  $\Delta\nu(0) = 4463.3013(40)$  MHz, while a joint fit with earlier Chicago Kr data gives  $\Delta\nu(0) = 4463.3012(23)$  (0.5 ppm). With  $f_\mu/f_p = 3.183338(13)$  this implies (a)  $\alpha^{-1} - 137 = 0.03619(30)$  (2.2 ppm) and (b) a proton polarizability  $\delta_N^{(2)} = -(4 \pm 4)$  ppm.

The hyperfine interval  $\Delta\nu$  of muonium can be determined with high precision by two microwave resonance methods, viz. (a) directly, by observing  $F = 1 \rightarrow F = 0$  transitions in "zero" external field,<sup>1</sup> and (b) from the frequencies of suitable Zeeman transitions in a strong external field.<sup>2</sup> Notwithstanding recent advances<sup>3</sup> in the latter technique, the direct method has several potential advantages. These are, however, largely compensated by the fact that a straightforward zero-field resonance<sup>1</sup> yields, for a given signal height, a much larger linewidth  $\Gamma$  than the high-field resonance (e.g., 1400 vs 520 kHz for 90% saturation), while the statistical uncertainty in locating the center of a Lorentzian goes as  $\Gamma/h$ . This large linewidth is connected, as we shall see later, with the three-level nature of the zero-field transitions.

We present here a novel technique which, while yielding linewidths narrower than the high-field resonance (in fact, narrower than the "natural" linewidth  $\Gamma_0 = 140$  kHz!), preserves all the advantages of the zero-field method. Our technique is, in virtue of this reduction in linewidth and of several lesser factors, statistically about 25 times more powerful than the (optimized) straightforward resonance in zero field. The latter bears roughly the same relation to the novel method as the Rabi resonance (single oscillating field) for atomic beams does to its modification by Ramsey (two separated oscillating fields).<sup>4</sup> In fact, this work was strongly inspired by that of Ramsey and his associates.

Although the exact treatment of the quantum mechanics underlying our method is extremely simple, let us first describe it qualitatively: As-