

ON THE SHAPE RESONANCES IN  $\text{NO}^-$  AND  $\text{N}_2^-$ Radu I. CĂMPEANU<sup>#</sup>*The University of Cluj, Faculty of Physics, Cluj, Rumania*

Received 28 June 1974

Revised manuscript received 24 September 1974

The method used by Koike and Watanabe to describe negative molecular ion formation is generalized for multi-waves states of the extra electron. The structure of the shape resonances in  $\text{NO}^-$  and  $\text{N}_2^-$  is discussed. For the  $\text{NO}^-$ -captured electron it is found that the  $d\pi$ -wave component increases with increasing resonance energy.

## 1. Introduction

Vibrational excitation by electron impact on diatomic molecules is now well understood [1]. It has become clear that at low energies (0–4 eV) the shape resonances play a major role in this process, the cross section for direct excitation being one or two orders of magnitude lower than for excitation via compound states.

Resonance scattering occurs through the entry of the projectile electron into the molecule  $\text{X}_2$  to form the compound state  $\text{X}_2^-$ , whereupon the nuclei start to move in the new potential, after a time the visiting electron is re-emitted, while the residual molecule is left in a distribution of vibrationally excited states. A powerful theoretical method for explaining the capturing mechanism is the use of configuration interaction [2]. Koike and Watanabe obtain in this way a capturing cross section formula (eq. (16) of ref. [3]) essentially equivalent to Breit–Wigner's one level formula. The evaluation of the transition matrix element involved in eq. (16) was performed in the molecular frame representation, under the presumption that the transition is a Landau–Zener type transition, which can occur at the crossing point between the adiabatic potentials of  $e + \text{X}_2$  and  $\text{X}_2^-$  systems. Their omission of the molecular rotation is a good approximation for molecules which form a compound state with a

short lifetime, as for  $\text{NO}$ ,  $\text{N}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ , but not for  $\text{O}_2$ . The final formula of ref. [3] is the following energy integrated capturing cross section:

$$\begin{aligned} \Sigma_{\text{capt}}^{lm} &= 2\pi^2 k^{-2} \Gamma g \\ &= \frac{4\pi^3 \mu \epsilon_i |V_{\text{ad}}^{lm}(R_c)|^2 |\chi_i(R_c)|^2}{\hbar^2 k [\partial(V_f - V_i)/\partial R]_{R=R_c}}, \end{aligned} \quad (1)$$

where  $\Gamma$  is the resonance width,  $k$  the wave number of the incident electron,  $\mu$  the reduced mass,  $\epsilon_i$  the energy separation between the vibrational energy levels of the neutral molecule,  $\chi_i(R_c)$  the vibrational wavefunction for the neutral molecule at the crossing point  $R_c$ ,  $V_f - V_i$  the difference in the adiabatic potentials,  $g$  the spin correction factor arising from the discrepancy of the spin multiplicity between the incident channel and the compound state:  $g = 2(2S' + 1)/(2s + 1)(2S + 1)$ ,  $s$ ,  $S$ ,  $S'$  being the spin momenta of the incident electron, the target molecule and the compound state, respectively.  $V_{\text{ad}}^{lm}$  is the adiabatic matrix element, depending on  $l$ , the orbital angular momentum quantum number of the captured electron and  $m$  the magnetic orbital quantum number. The general form of  $V_{\text{ad}}^{lm}$  is given by eq. (24) of ref. [3] and the calculation in that case was performed for  $l = 2$ , which is the only partial wave accepted by the  $\text{O}_2^-$  ground state symmetry.

We may generalize the  $V_{\text{ad}}$  matrix element calculation for the extra electron in a mixture of different waves. In the molecular frame representation, after

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summing over  $m$ , we get:

$$V_{\text{ad}} = 0.462\alpha \sum_{l \neq 0} a_l \frac{k^l \zeta^{5/2-l}}{1 \cdot 3 \cdot 5 \cdots (2l+1)}, \quad (2)$$

where  $\alpha$  is the electronic polarizability,  $a_l$  the mixing coefficient and  $\zeta = (2\mu|E_{\text{aff}}|)^{1/2}$ ,  $E_{\text{aff}}$  being the adiabatic electron affinity,  $E_{\text{aff}}$  and  $E_{\text{res}}$  (the incident energy) and implicitly  $\zeta$  and  $k$  are small in our problem and so the terms under the summation  $\sum_{l \neq 0}$  of eq. (2) are very small. Because they are positive too, we may approximate the square of the sum in the modulus with a sum of squares.

It follows that substituting eq. (2) into eq. (1), we obtain:

$$\begin{aligned} \Sigma_{\text{capt}} &= 2\pi^2 k^{-2} g \Gamma, \\ \Gamma &= 1.345 \frac{\mu \epsilon_f \alpha^2}{\hbar^2} \frac{|\chi_i(R_c)|^2}{[\partial(V_f - V_i)/\partial R]_{R=R_c}} \\ &\times \sum_{l \neq 0} a_l \frac{k^{2l+1} \zeta^{5-2l}}{1 \cdot 9 \cdot 25 \cdots (2l+1)^2}. \end{aligned} \quad (3)$$

We shall apply formula (3) to a long-lived shape resonance ( $\text{NO}^-$ ) and to  $\text{N}_2^-$  which has a lifetime comparable to the vibration time. We have chosen these examples because both present some interesting features.

## 2. Nitric oxide

The structure of the shape resonance in  $\text{NO}^-$  was discussed by Spence and Schulz [4], the spectroscopic constants for NO are given by Herzberg [5] and the electronic polarizability by Scharpen et al. [6].

For the potential gradient  $[\partial(V_f - V_i)/\partial R]_{R=R_c}$  determination, the Morse function may be used:

$$V(R - R_e) = D_e \{1 - \exp[\beta(R_e - R)]\}^2, \quad (4)$$

where  $R$  is the internuclear separation,  $R_e$  the equilibrium value,  $D_e$  the dissociation energy referred to the minimum of the curve and  $\beta = w_e(2\pi^2 c \mu / D_e \hbar)^{1/2}$ ,  $w_e$  being the vibrational frequency.

In atomic units, the constants involved in eq. (3) are:  $\epsilon_f = 0.22$  eV,  $E_{\text{aff}} = 0.02$  eV,  $\alpha = 22.15 a_0^3$ ,  $g =$

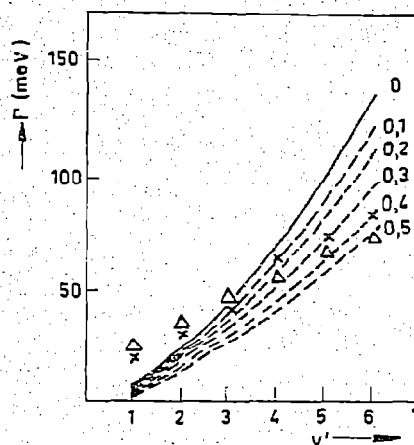


Fig. 1. Calculated width of the resonance levels  $v'$  in  $\text{NO}^-$  for different  $p\pi$ - $d\pi$  mixtures represented by the mixing coefficient  $a_2$ . The experimental widths are given by ref. [4] (the triangles) and by ref. [11] (the crosses).

$$3/2, |\chi_i(R_c)|^2 = 1.1/a_0 \text{ and } [\partial(V_f - V_i)/\partial R]_{R=R_c} = 0.13 \text{ eV}/a_0.$$

The lowest vacant orbital of the ground state of NO is a  $3p\pi$  type orbital (in united-molecule notation) and the branching ratio's observation [4] confirm the  $p\pi$ -state of the extra electron. Bardsley and Read [7] have pointed out that in resonance formation and decay the partial waves which are mixed are  $p\pi$  and  $d\pi$  waves, the  $p$ -wave component being more efficient.

Fig. 1 presents our theoretical width for different mixtures of  $p\pi$  and  $d\pi$  waves. Their magnitude, in agreement with the experimental width, confirm the vibrational structure of the shape resonance. The comparison of the theoretical and experimental resonance energy ( $v'$  or vibrational quantum number) dependence indicates, interestingly, the increase of the  $d\pi$  wave with the increasing resonance energy (see the mixing coefficient ratio in table 1). This observation was already noted [7] for CO, which has a similar behaviour.

For the first and second quantum numbers, the experimentally observed widths are almost entirely caused by the instrumental resolution.

Using the experimental width one may calculate with eq. (3) the electron capturing integrated cross section. The results are listed in table 1, and indicate a slow decrease with increasing vibrational quantum number.

Table 1

Electron capturing integrated cross sections (in  $a_0^2$  eV) and mixing coefficient ratio  $a_2/a_1$  for the  $v' = 3-6$  resonant vibrational levels of  $\text{NO}^-$ . Resonant vibrational energy measured from the ground state of  $\text{NO}$ , is obtained from ref. [4]. First line corresponds to the experimental width from ref. [4] and the second from ref. [11]

$v$	$E_{\text{res}}$ (eV)	$\Sigma_{\text{capt}}^{l=1,2} (a_0^2 \text{ eV})$	$a_2/a_1$
3	0.44	8.57	0
		9.83	0.06
4	0.6	9.6	0.33
		8.5	0.14
5	0.76	8.89	0.61
		8.27	0.37
6	0.92	7.71	1.10
		7.2	0.67

### 3. Nitrogen

The shape resonance in  $\text{N}_2^-$  above 1.8 eV, with its lifetime comparable with the vibrational time, presents an ambiguous behaviour, thus stimulating theoretical interest. The ambiguity arises from the fact that if one presumes a vibrational structure of the shape resonance, as for  $\text{NO}^-$  (i.e., the compound state has enough time to vibrate several times before autoionizing), the peak positions in the energy dependence of the vibrational excitation cross section are different for different exit channels. The peaks shift to higher energies for higher vibrational states of the neutral molecule. Anyway, the manifestation of a particular resonance may be quite different in different inelastic channels. The shape parameter [2]  $q$ , which indicates the difference between the peak position and the resonance energy, is proportional to the width. For very large widths as for  $\text{N}_2^-$ , we expect to have an experimentally perceptible shift.

The results represented in fig. 2 are obtained with eq. (3), with the use of the early shape resonance calculations [8,9], and with Herzberg's spectroscopic constants for  $\text{N}_2$ . A remarkable agreement is obtained for the calculated  $[\partial(V_f - V_i)/\partial R]_{R_c} = 6 \text{ eV}/a_0$  and  $|\chi_i(R_c)|^2 = 16.1/a_0$  with the empirical values of Herzenberg and Mandl [10]. The other constants are:  $\epsilon_i = 0.29 \text{ eV}$ ,  $E_{\text{aff}} = -1.89 \text{ eV}$ ,  $\alpha = 23.4 a_0^3$ ,  $g = 2$  and  $l = 2$ . The resonance energies are considered to be the peak energies in the elastic scattering [11] ( $0 \rightarrow v \rightarrow 0$ ).

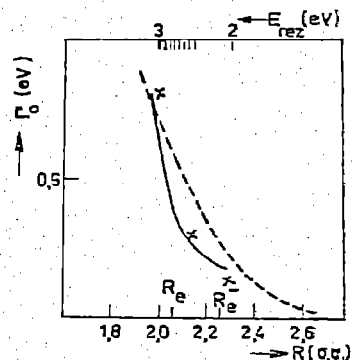


Fig. 2. Calculated width versus resonance energy and internuclear separation in  $\text{N}_2^-$ . The full line is the present result, the dashed line from ref. [8] and the crosses from ref. [9].

Our results demonstrate that the autoionizing levels in  $\text{N}_2^-$  are almost completely overlapped, i.e., only the  $v = 0$  level is separated by 50 meV from the other overlapping levels. This shape resonance structure may be an explanation for the dip observed by Schulz (see fig. 6 in ref. [12]) in representing the sum of the vibrational cross sections versus electron energy.

The electron capturing integrated cross section is evaluated to be  $53.6 a_0^2 \text{ eV}$  for the 1.89 eV level and  $248 a_0^2 \text{ eV}$  for the "continuum".

If the possibility of only one vibration is considered before autoionization, the "boomerang" model [8] necessarily includes the variation of the width  $\Gamma$  with the internuclear separation  $R$ . But as it was pointed out by Krauss and Mies [9], there is immediate correlation between the  $R$  dependence and the resonance energy dependence on the left of the  $\text{N}_2^-$ -equilibrium internuclear distance. Fig. 2 presents both dependences. Our  $E_{\text{res}}^{l+1/2}$  dependence is in perfect agreement with the ab initio calculation of Krauss and Mies.

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