

ISOTOPIC EFFECT IN THE RESONANCE DISSOCIATIVE CAPTURE OF AN ELECTRON AND QUASISTATIONARY STATES OF MOLECULES

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A quasi-stationary state of a molecular ion AB- can be formed if an electron collides with a molecule AB. This is a "vertical" transition according to the Frank-Condon principle. So AB- is formed in a non-stable state and can dissociate into a negative ion and atom. But the time of dissociation is relatively large (about 10^-13 sec) due to the large mass of the nuclei, so the backward transition AB- -> AB+e can take place. During the backward decay the nuclei preserve their position and relative velocity, so after decay the molecule AB can be formed in an excited vibrational state or even dissociate and the detached electron will have consequently lower energy than the initial one. Which of the two processes dominates depends on the relation between the mean lifetime of the quasi-stationary state AB- (or on the width of its energy level Gamma) and the time of dissociation tau.

The cross section peaks for the resonance capture occur usually at energies about 10 eV. So the maximum cross section must be of the order lambda^2 (lambda - the wave length of the electron) i. e. 10^-16 cm^2. But the experiment gives the maximum cross section of negative ions formation about 10^-19 - 10^-20 cm^2. Such discrepancy can be explained by two reasons.

Firstly, there is some uncertainty Delta R in the internuclear distance R and therefore the uncertainty Delta E in the energy of the resonance capture. If the latter is much more than Gamma then a very narrow resonance peak with a maximum of the order 10^-16 cm^2 must be averaged over the whole interval Delta E of the resonance capture energies which is of the order of some eV. Such smoothing sharply decreases the maximum cross section.

Secondly, after the capture the great part of the formed ions can undergo the backward decay before the complete dissociation, so the probability of the negative ion formation per capture can be very small. This probability can be calculated in the "quasi-adiabatic" approximation if the width Gamma(R) is given according to the formula

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w = exp(-2/h * integral from t(R_0) to t(R_1) of Gamma dt) = exp(-2 * Gamma_bar * tau/h),

which is a natural extension of the usual adiabatic approximation to the quasi-stationary (auto-ionising) states. Here R_0 is the mean internuclear distance for AB, R_1 is the crossing point of the potential curves AB and AB-, Gamma_bar is the mean width of the curve AB- in the region (R_0, R_1). We can expect that the maximum cross section for the negative ion formation is some orders lower than the resonance capture cross section if 2 * Gamma_bar * tau/h is of the order 10 or more. This corresponds to an energy width of the order of 0.1 eV which looks quite reasonable if one assumes that this value is several times more than that for atoms.

One can consider the same reaction but with the isotopically substituted molecule A'B' in order to decide which of these two possibilities takes place. Then the process of capture remains almost unchanged (there is only a small difference in Delta R) but the time of dissociation tau can be changed essentially and therefore the probability of the negative ion formation also will change drastically due to the exponential dependence.

One can expect the most striking effect in the reaction e + H2 -> H- + H. The resonance maxima in this case were found by Dukel'sky and Khvostenko [1] and later by Schulz [2] at an energy 14 eV (width ~ 1 eV) and apparently two unresolved maxima at 10 and 11.5 eV (width ~ 2 eV). The first of these maxima apparently corresponds to the asymptotic state H(2s, 2p) + H-, the second and third to the states Sigma_u and Sigma_g of H(1s) + H-. The time of dissociation increases by sqrt(2) if we substitute H2 by D2 and therefore we

can expect a strong decrease of the resonance peaks for D_2 .

The experiments of Fite and Brackman [3] where the dissociative capture of electrons in O_2 was measured at various temperatures give an indirect confirmation of the importance of backward decay. They found a shift of the maximum cross section to the lower energies and an increase of the absolute magnitude of the maximum at $T = 2100$ °K, when the first three vibrational levels were appreciably excited. This can be explained by the increase in the probability of capture at large R . The energy of resonance capture then becomes lower, the time of dissociation decreases and so does the probability of backward decay. For oxygen the width ΔE of the resonance maximum is large (about 5 eV), so the potential curve for O_2^- in the vicinity of R_0 is very steep and the effect must be large. The excitation of rotational states also increases R_0 and acts in the same direction. Otherwise (in the case of a small backward decay probability) one would expect the decrease of the maximum due to the increase of ΔR and therefore the larger smoothing of the ideal resonance peak.

Thus 1) The position of the maximum and its absolute magnitude gives a possibility to obtain the position, steepness and width of the potential curve AB^- in the vicinity ΔR of the R_0 .

2) The observations at high temperatures make it possible to take into account the contribution of excited vibrational and rotational states and enlarge the region ΔR .

3) The isotopic effect and the measurement of the energy of secondary electrons allow us to obtain the potential curve of AB^- and the width $\Gamma(R)$ for larger R up to R_1 , the crossing point of both curves.

4) The properties of the quasi-stationary potential curve of AB^- can be investigated also in other reactions such as the associative detachment (the inverse process), charge exchange and others.

5) The investigation of quasi-stationary states of molecules is also possible by observation of resonance scattering of photons by molecules and photo-dissociation.

It must be stressed that at present we know very little about the auto-ionising states of molecules. The calculations here are very difficult due to the absence of a variational principle. It is especially difficult to estimate the lifetime of these states. Meanwhile they are very important in various collisions, chemical reactions etc. Therefore it is important to use all the experimental possibilities for an investigation of these states.

In conclusion I wish to make my acknowledgements to Professors Fite, Dukel'sky, Drukarev and Dr. Dubrovsky for discussions of topics in connection with this paper.

(After this paper was written we received a preprint [4] where it is announced that the dissociative capture in D_2 is several times lower than that in H_2 . The authors remark that "this unexpected result is difficult to understand". The shift of the resonance maximum in O_2 is also discussed. Neglecting the backward decay the authors made a calculation and obtained a shift in opposite direction. They note that "there is something drastically wrong with the elementary theory".)

References

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