PHOTODISSOCIATION SPECTROSCOPY AND PREDISSOCIATION PATHWAYS IN HCN AND DCN

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A detailed study of the predissociation H(D)CN ($\tilde{C}^1A'$)→H(D)+CN ($B^2\Sigma^+$), which includes analysis of absorption and photofragment fluorescence excitation spectra and measurements of the relative quantum yields and polarizations of the CN(B→X) fluorescence following excitation into different vibronic levels in the parent molecule, has been used to help characterise the nature of the excited electronic parent molecular states and provide information on the topography of the potential surfaces over which the predissociation proceeds.

In both HCN and DCN, the quantum yields and polarization ratios of CN(B→X) fluorescence tend to decrease as the energy of the absorbed photon is reduced, indicating a gradual decrease in the rate of predissociation as the energy falls toward threshold. The detailed behaviour is not monotonic however, and the rates of predissociation from individual vibronic states are sensitive to the vibronic mode composition in the level initially populated.

The photofragment fluorescence excitation spectra from HCN and DCN are displayed in figs. 1 and 2; all the major vibronic bands can be attributed to progressions in the $\tilde{C}^1A'$ state. The absence of any progressions which involve excitation of the C—H stretching mode ν_1' in HCN contrasts with the structure observed in the corresponding spectrum for DCN, where progressions with $\nu_1 \leqslant 2$ are quite sharp and spectral line broadening only becomes pronounced when $\nu_1' = 3$. This has led to the suggestion that the rate of predissociation in HCN is so greatly accelerated by excitation of ν_1' that the corresponding spectral features merge into a continuum. Indeed, comparison of the absorption and fluorescence excitation spectra of HCN reveals an enhanced contribution from an underlying continuum at $\lambda \sim$ (130—135) nm (see fig. 2) and it is in this region that the $(1,\nu_2',0)$ progression, if it were resolved, would be most intense.
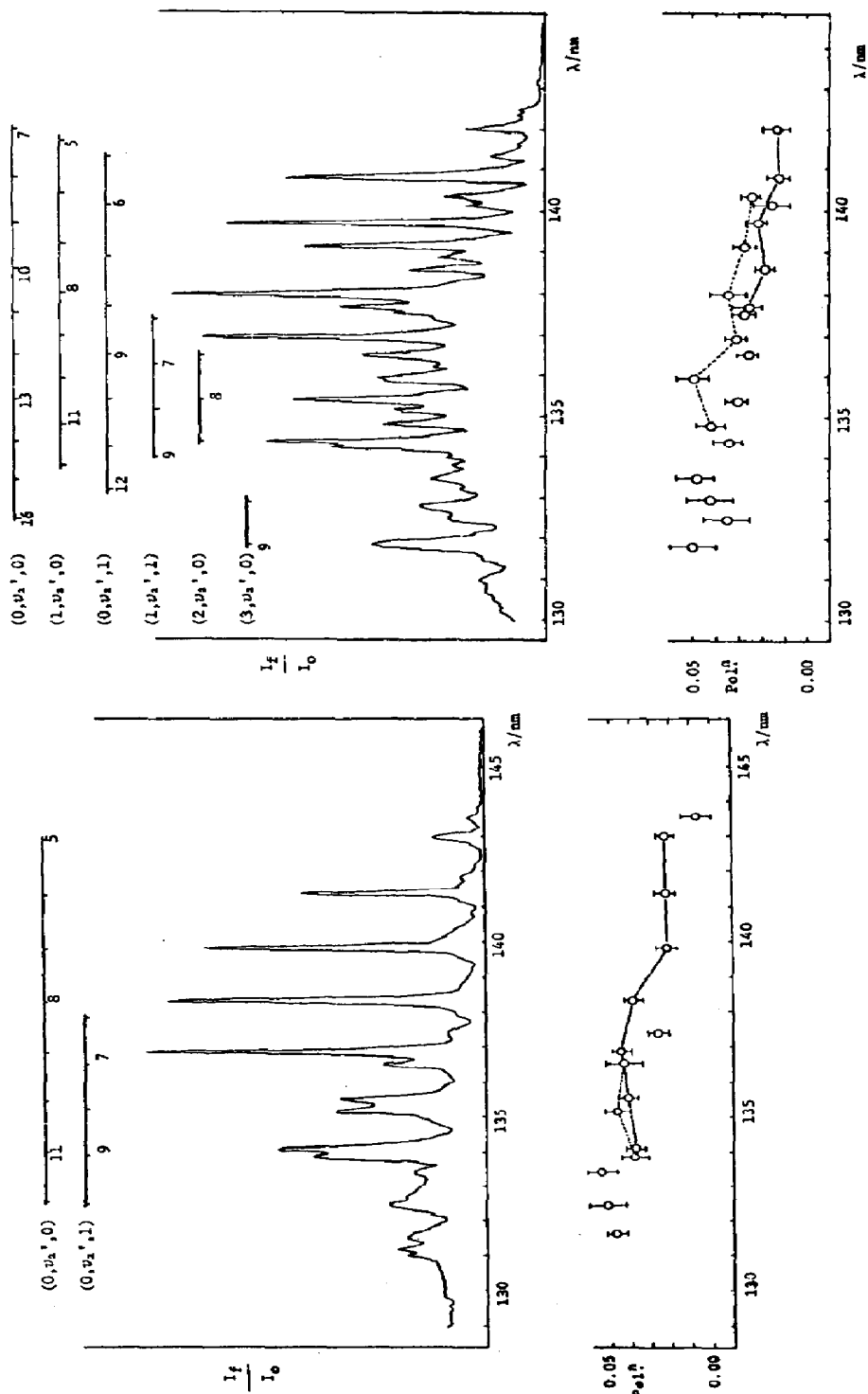
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Fig.2   Photofragment excitation spectrum of DCN, with measured polarizations.

Fig.1   Photofragment excitation spectrum of HCN, with measured polarizations.

The isotope sensitivity of the rates of predissociation in HCN and DCN can be understood in terms of a tunnelling mechanism out of the $\tilde{C}^1A'$ state, since penetration through the non-classical region would be reduced by deuteration, but enhanced by excitation of v_1'. By combining the results for the vibrational energy disposal, (which lead to an estimate of the steepness of the repulsive potential between the separating fragments), with the observed isotope effect on the rates of predissociation, (which leads to an estimate of the potential barrier through which tunnelling may proceed), it has been possible to map the contour of the potential surface along the reaction coordinate (assumed to be Q_1, the H(D)-CN distance) (see fig. 3).

If the tunnelling mechanism provided the only predissociative pathway, the isotopic sensitivity would be greatest when $v_1' = 0$, since this would correspond to the maximum barrier width. In fact, the rates of predissociation from levels with $v_1' = 0$ in HCN and DCN, as reflected by the observed line widths, polarization ratios and relative CN(B) quantum yields, are very similar, and an alternative pathway must still be available when the tunnelling route is too slow to compete, i.e. when $v_1' = 0$ in HCN and when $v_1' \leqslant 2$ in DCN.
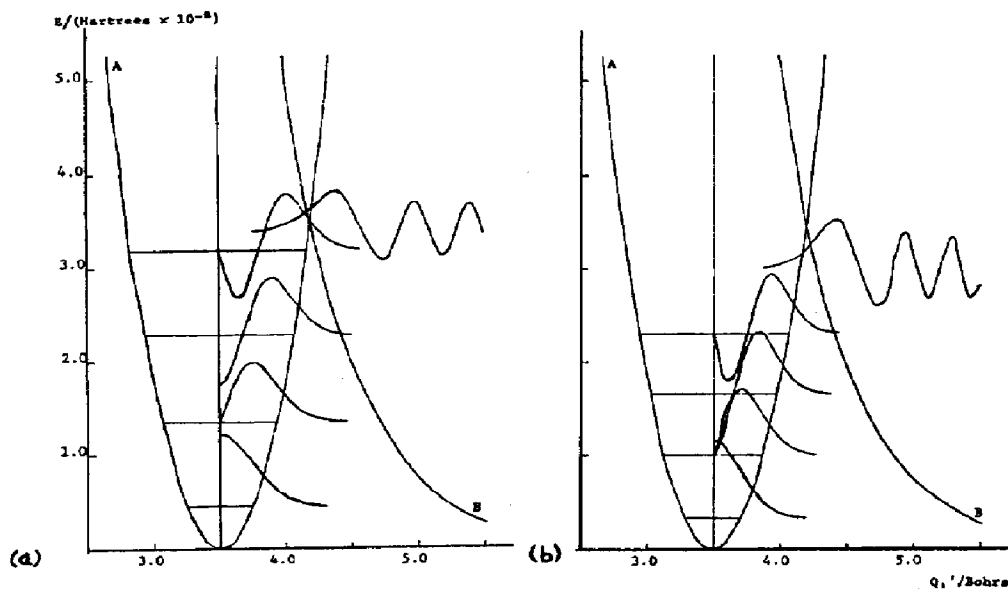

Fig. 3. Bound and continuum potential energy functions for (a) HCN and (b) DCN, showing variation in the Franck-Condon overlap with isotopic substitution: A, bound simple harmonic oscillator function with (a) $v_1' = 2000$ cm^{-1} and (b) $v_1' = 1450$ cm^{-1}; B, exponentially repulsive function of the form $V - V_0 \exp(-Q_1/L)$, where L = 0.5 Bohr and V_0 = 140 Hartrees.