Photoabsorption and photodissociation in molecular nitrogen

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Declaration

This thesis is an account of research undertaken between February 2006 and November 2010 at The Research School of Physics and Engineering, The Australian National University, Canberra, Australia.

Except where acknowledged in the customary manner, the material presented in this thesis is, to the best of my knowledge, original and has not been submitted in whole or part for a degree in any university.

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Abstract

The photoabsorption and photodissociation of molecular nitrogen at extreme-ultraviolet wavelengths has been precisely modelled by solution of the coupled Schrödinger equation, for the purposes of elucidating the spectroscopy and predissociation dynamics of N_2 and for practical application to its photochemistry. The physically realistic model is capable of reliable extrapolation beyond the database of spectroscopic information necessary for its construction, to energies in the range of 100 000 to 118 000 cm^{-1} and, with some caveats, beyond this; and for any temperature, rotational state, and isotopomer of N_2. The model simulated spectra have an effectively-infinite resolution, and reproduce the rotational level energies of all electric-dipole-allowed $^1\Pi_u$ and $^1\Sigma_u^+$ states, and their absorption f-values, to spectroscopic accuracy over its entire range. The predissociated lineshapes of calculated transitions are accurately reproduced, as is the background continuum, even where a dissociation limit is crossed.

The highly perturbed spectrum is shown to arise from multi-channel effects which can only be reproduced by a coupled treatment which includes the effects of homogeneous and heterogeneous interactions. Unbound dissociative states are permitted in the model formulation and a complex of $^3\Pi_u$ and $^3\Sigma_u^+$ states is shown to be responsible for the predissociation of singlet levels via spin-orbit interaction. The spectroscopic parameters of triplet states, and the variation of $^1\Pi_u$ predissociation rates over multiple orders of magnitude has been accurately modelled for all isotopomers and energies up to 111 000 cm^{-1}. The transformation of the calculated dissociative wavefunctions into a basis of asymptotically well-defined atomic states allows for the calculation of their predissociation branching ratios. New and accurate determinations have been made of potential-energy curves for the coupled states, the off-diagonal matrix elements that mix them, and the electronic transition moments responsible for their optical excitation, including, in some cases, their dependence on internuclear distance.

New supporting laboratory measurements of rotationally-resolved absolute f-values and predissociation linewidths have been made for many transitions, some of which have not been previously observed. These various experiments employ synchrotron and laser radiation as well as electron-impact excitation, and make detections by means of a grating spectrometer, Fourier-transform spectrometer, and the detection of photofragments. Analysis of these studies is facilitated by the coupled-channels modelling, which is then informed by the resulting new data.

The characteristics of the coupled-channels model are an ideal match to the immediate need for N_2 spectra by photochemical modellers of planetary atmospheres, because of its realistic extensibility to variable real-world conditions. An application of the model to the atmosphere of Titan is presented here, which explains the unusual observed ratio of nitrogen isotopes in terms of the details of N_2 photoabsorption. Another use of modelled spectra is presented here, for the analysis of the terrestrial dayglow. The applicability of the coupled-channels model is quite broad and further investigations which utilise it are underway.

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