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Radioastronomical frequency for interstellar NH⁺

SOME spectroscopic frequencies may be calculated more accurately than laboratory experiments can measure them. *Ab initio* molecular orbital calculations can be used to compute molecular properties, but none as accurately as Λ-doubling. This effect gives rise to splittings of molecular energy levels of diatomic molecules and transitions between the Λ-doublets are the sources of some of the most important radioastronomical spectral lines. Here we consider the as yet unobserved but very likely instellar species NH⁺.

Very crudely, Λ-doubling may be thought of as an effect of electron slip as the molecule rotates; the electrons lagging somewhat behind the rotating nuclear frame. This results in the energies of degenerate Π molecular energy levels becoming different, with an energy separation which increases as the rotational quantum number increases. Formally the effect may be described as the influence of Σ electronic states on Π states. The interaction, which is zero to a first approximation, is dominated by spin–orbit coupling, giving non-zero matrix elements between Σ and Π states.

The well-known astrophysical source, OH, was the subject of calculations[1] which would now be thought of as relatively crude, but in wave numbers the agreement with experiment is impressive (observed 0.0788 cm⁻¹: calculated 0.0810 cm⁻¹). This encouraging result was, in a sense, fortuitous because the origin of the splitting in OH is particularly simple, being an example of Van Vleck's approximation of pure precession where the ²Π electronic ground state is only seriously influenced by a single ²Σ⁺ state.

The case of CH is more complex as several states of ²Σ⁺ and ²Σ⁻. symmetry have to be considered, but agreement with experiment[3–5] is close enough for the computations to be within a few MHz of the observed astrophysical frequency.

We have now extended this work to the species, NH⁺, where a further complication enters the calculations. In this case we have to consider not only interacting ²Σ⁺ states but also ⁴Σ⁻ states. Configuration interaction wave functions and potential energy curves were calculated for the $X^2\Pi$, $a^4\Sigma^-$, $A^2\Sigma^-$ and $C^2\Sigma^+$ states of NH⁺ using the Alchemy system of computer programs[6]. Using these wave functions and potential energy curves the interaction between the X ²Π state and the a ⁴Σ⁻ state was treated numerically, whilst the interaction with the ²Σ⁺ states was calculated using second-order perturbation theory. It is important that because of the influence of the ⁴Σ⁻ state, the Λ-doubling in the $X^2\Pi$ state of NH⁺ cannot be interpreted in terms of the conventional constants p and q and each rotational level must be treated separately.

The results of these calculations predict Λ-doubling in the lowest rotational level of ¹⁴NH⁺ to be 13,625 MHz. This may be compared with the best laboratory experimental value of $13,520 \pm 300$ MHz for which special measurements were made[7].

The splittings to be expected in ¹⁴ND⁺ and ¹⁵NH⁺ together with values in excited rotational levels for which accurate experimental measurements are not available will be published elsewhere with fuller details of this work.

Our predicted frequency of NH⁺ is within the range of available radiotelescopes and the calculations could provide the first example of a case where theory has predicted a radiosource rather than merely confirmed its identification.

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Irreversibilities in the mechanism of photoelectrolysis

PHOTODECOMPOSITION of water using semiconducting electrodes is being widely investigated. Using a combination of theoretical methods and experimental results we have analysed the sequential processes involved in this phenomenon and show here that several steps are irreversible. Some of the consequences of these irreversibilities are discussed. A theory of electronic charge transfer between electrodes and aqueous electrolytes, based on an equilibrium approximation by Marcus[1], seems to be valid for metal electrodes. Gerischer[2] has considered both metal and semiconductor electrodes and concluded that in general the electron is isoenergetically injected (tunnels) from the occupied band state of the electrode into an unoccupied state of the electrolyte. Rearrangement of the molecular environment then occurs, irreversibly changing the energy of the electronic state of the electrolyte. Finally, reverse tunnelling from the relaxed state back into the electrode may occur.

The two states of occupancy in the electrolyte constitute a redox couple. For metals the forward and reverse currents become equal as equilibration occurs; thus, the Fermi level of the metal adjusts to the redox potential of the redox couple of the electrolyte. For semiconductors, electronic charge transport involving different bands (electrons in the conduction band and positive holes in the valence band) have been separately considered[2]. This situation can lead to either an equilibrium or a non-equilibrium charge transfer process between semiconductors and electrolyte. The equilibrium approximation frequently appears in analyses of electronic charge transport between semiconductors and electrolytes. In particular, Gerischer[3] has invoked the quasi-Fermi level concept to describe the charge carrier concentrations at the semiconductor–electrolyte interface under illumination.

Here we point out some irreversible aspects of charge transfer across semiconductor–electrolyte interfaces for photogenerated minority carriers, and emphasise the importance of these irreversibilities in explaining photoelectrolysis[4–7] and the mechanism of the operation of the photochemical diode[8]. Furthermore, we believe that as a consequence of these irreversibilities, the quasi-Fermi level concept and the associated thermodynamic arguments are of limited validity for high efficiency photoelectrolysis. Irreversibility, has previously been proposed to explain reduction of ferricyanide at a ZnO semiconductor electrode[9].

The energy level diagram for the n-type semiconductor electrode–aqueous electrolyte interface involved in photoelectrolysis is shown in Fig. 1. The essential features of the semi-conductor–electrolyte junction are from Nozik[10]; the electronic states of water are from Williams *et al.*[11]. The bending of the conduction and valence band edges, E_c and E_v respectively, are determined by the space charge arising