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学 位 論 文 題 目　　Accurate ab initio theoretical studies of rovibronic

　　　　　　　　　states of some simple diatomic molecules

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Fundamental diatomic molecules and their rovibronic and ionic states have been paid an interest both experimentally and theoretically for so many years. Experimentally, there have been so many rotationally resolved absorption and emission spectra of diatomic molecule using grating, laser and so on. There have also been many spectra for the ionic states using photoelectron light source, and recent development in the photoelectron spectroscopy such as ZEKE, or PFI-PE, rotationally resolved spectra have been observed for those ionic states. There are also many theoretical studies using ab initio molecular orbital method. Fundamental diatomic molecules and their electronic excited states have been studied by using the configuration interaction method for a few decades. Recent development of molecular orbital theory and fast computer has made it possible to calculate the vibrational and rotational levels as well as electronic states more accurately. It is now possible to reproduce experimental data and the agreement between experimental data and theoretical results is very excellent and quantitative comparison of other properties is also possible. Theoretical calculations can also give very good prediction to for the states with no experimental data available. As both experiments and calculations become more accurate, calculated results with less accuracy become insufficient, and more accurate calculations are expected, but there are still few accurate calculation enough to explain experimental data quantitatively. In the present theoretical studies, accurate calculations were performed for several diatomic molecules and their ion, and their rovibrational levels.

In their accurate calculations, very large basis set, such as augmented quadruple zeta basis set, is used. Multireference configuration interaction (MRCI) calculations were performed for several electronic states of diatomic molecule. To describe properly the anti-bonding nature of molecular orbitals, valence-type-vacant(VALVAC) orbital method is used. The method requires only a single Fock matrix generation, and provides them with a proper anti-bonding nature of molecular orbitals. These orbitals are used as a reference space in the MRCI. In this method, they do not need to solve the state-averaged MCSCF. With a single set of molecular orbitals obtained by VALVAC method, the accurate potential energy and dipole moment functions both for the ground state and for the excited states are obtained. All the calculated results are compared with recent experimental data, which are in excellent agreement.

The topics and their summaries of the results are as follows.

(1) Accurate potential energy and transition dipole moment curves for several electronic states of CO^+.

Ab initio MO studies are performed for several doublet and quartet states of CO^+ using the multi-reference configuration interaction method. The neutral ground state of CO is also calculated. The following properties are compared with available experimental data.

(i) Low-lying electronic states, their rovibrational levels of each state up to the dissociation limit, and spectroscopic constants.

Adiabatic potential energy curves of several doublet and quartet states are calculated, and the vibrational levels are calculated using the potential energy curves. Spectroscopic constants, such as R_e, ω_e and $\omega_e x_e$ are obtained. For example, for the $X^2\Sigma^+$ state, the calculated R_e, ω_e and $\omega_e x_e$ are 1.1151 Å, 2214.6 cm^{-1}, and 14.75 cm^{-1}. Corresponding recent experimental values of R_e, ω_e and $\omega_e x_e$ are 1.119 Å, 2215.1 cm^{-1}, and 15.27 cm^{-1}. Calculated spectroscopic constants well reproduce the recent experimental data.

(ii) v dependence of rotational constant B_v.

The rotational constant B_v is obtained for each vibrational level. Rotational constants such as B_e, and α_e are calculated. The calculated B_e, and α_e are 1.981 cm^{-1}, and 0.0234 cm^{-1}. Corresponding experimental values are 1.9798 cm^{-1}, and 0.0202 cm^{-1}. Calculated rotational spectroscopic constants also well reproduce experimental data.

(iii) The transition dipole moment functions and the lifetimes of the vibrational levels.

Transition dipole moment functions between the electronic states are also calculated. The lifetimes of the vibrational levels are evaluated by obtaining the Einstein's A coefficients, and the lifetimes are compared with experimental data. Calculated lifetime of the vibrational level $v=0$ of the $B^2\Sigma^+$ state of CO$^+$ is 56.40 ns. Corresponding experimental value is 57.1 ns. This agreement implies that the calculated Einstein's A coefficients to the lower electronic state are accurate.

(2) Ab initio studies of several excited states of CO$^+$.

The adiabatic potential energy curves of the $X^2\Sigma^+$, $A^2\Pi$, $B^2\Sigma^+$, $C^2\Delta$, $D(2)^2\Pi$ and $3^2\Pi$ states of CO$^+$ are calculated, and the vibrational levels of each state and spectroscopic constants are obtained. The vibrational levels of the $D(2)^2\Pi$ and the $3^2\Pi$ states are particularly focused on. Adiabatic potential energy curves of the $D(2)^2\Pi$ state shows that there is an avoided crossing between the $D(2)^2\Pi$ and the $3^2\Pi$ states. The splitting is about 1200 cm^{-1}. Calculated vibrational levels using adiabatic potential energy curve show that here are only 3 vibrational levels. However, experimental data shows a vibrational progression of the $D(2)^2\Pi$ state; the progression reaches up to $v=9$. Experimentally obtained $v=9$ level lies well above the barrier of the adiabatic potential energy curve of the $D(2)^2\Pi$ and the $3^2\Pi$ state, too. Thus, if the experimental assignment to the vibrational progression is correct, the vibrational levels above $v=2$ have to be on the diabatic potential energy curve. The experimental data shows that the diabatic representation of the states is a good approximation to describe the rovibrational levels. To confirm it, the spectral intensities and their bandwidths of the vibrational levels on the diabatic potential energy curve are calculated

and compared with experimental data.

(3) Accurate potential energy and transition dipole moment curves for several electronic states of N_2^+.

Ab initio MO studies are performed for several doublet and quartet states of N_2^+ using the multireference configuration interaction method. The following properties are compared with available experimental data. Spectroscopic constants, such as R_e, ω_e and $\omega_e x_e$ are obtained. For the $X^2\Sigma_g^+$ state, the calculated R_e, ω_e and $\omega_e x_e$ are 1.119 Å, 2212.3 cm^{-1}, and 16.87 cm^{-1}. Corresponding recent experimental values of R_e, ω_e and $\omega_e x_e$ are 1.11642 Å, 2207.0 cm^{-1}, and 16.10 cm^{-1}. Also in this case, the agreement between the calculated results and experimental data is excellent.

(3) Rovibrational studies the neutral CO and investigations of rotational temperature of CO in the sun.

Rovibrational levels and their spectral intensities for absorption up to $v=9$ and $J=150$ are calculated for the $X^1\Sigma^+$ state of CO. Calculated spectral intensities are compared with experimental data observed from the sun by satellite. A few different rotational temperatures are assumed to calculate the spectra, because the spectral intensities depend on rotational temperature. Calculated spectral intensities are compared with experimental data. Using the calculated result with known rotational temperature, rotational temperature of CO in the sun is estimated to be about 5000 K.

論文の審査結果の要旨

　本論文は、一酸化炭素とその陽イオンおよび窒素分子イオンの分子基礎定数を第一原理量子化学計算によって正確に計算し、光電子スペクトル、回転振電発光・吸収スペクトルの解析・予測を行い、実験的に絶対値を得難い回転・振動・電子遷移に対するアインシュタイン A 係数と B 係数を高い精度で理論計算できることを実証した。

　2 原子分子の分光学の歴史は古いが、レーザーやシンクロトロン放射を用いた分光学、人工衛星上の観測などによって、高い励起状態まで詳細な研究が報告されるようになってきた。これら分子分光データは地球・惑星の大気や星間物質の遠距離計測に必要な基礎的物理量である。中でも吸収・発光の遷移確率は定量的遠距離計測に不可欠な量であるが、実験的に絶対値を決定するのが困難である。本研究では、分子軌道理論に基づく多電子理論計算法である多参照配置間相互作用(MR CI)法を用いて、分光定数と遷移確率を高精度に計算することに成功している。計算精度の向上のために、1 電子基底関数には高い軌道角運動量(l =4)の関数を加えた関数系を選択し、また計算精度を広い結合距離範囲で高く保つために、参照電子配置を構成する活性軌道を「原子価型空軌道決定法」によって求めている。得られた断熱ポテンシャルエネルギー曲線上の分子の振動準位とその波動関数を各回転量子数 J 毎にシュレディンガー方程式を数値的に解いて求め、分子分光定数と遷移確率を計算している。一酸化炭素分子陽イオン CO^+ の基底状態 $X^2\Sigma^+$ 状態の振動準位間隔と回転定数の振動量子数 υ 依存性は、 υ =41 に到るまで本研究の計算値は最近の実験値とよく一致し、その結果断熱近似がわずかに破れている現象を明らかにする事に成功している。励起状態 $A^2\Pi$, $B^2\Sigma^+$ の分光定数も精度高く計算されたが、特に、各振動準位の放射寿命は、実験データのある場合についてはその誤差内で計算値は一致した。また、最近観測された $D^2\Pi$ 準位の振動プログレッションは、断熱近似では解析できず、2 準位の透熱準位間の相互作用を正しく考慮して始めて理解できることを定量的に示した。

　さらに、電子基底状態一酸化炭素分子 CO の振動回転遷移確率の量子数依存性を高い(υ , J)まで計算し、NASA が人工衛星上で観測した太陽大気中 CO の振動回転吸収スペクトルを解析し、観測された分子の振動・回転温度を見積もることができることを示した。この計算において、振動回転遷移確率の回転量子数 J 依存性を正しく見積もるためには、各 J 毎に振動波動関数を求めなければならないことを定量的に明らかにした。同様の計算を窒素分子イオン N_2^+ についても行い、大気放電中、可視部に観測される窒素分子陽イオン N_2^+ の発光である $X^2\Sigma_g \leftarrow A^2\Pi_u$ 遷移の自然放射寿命の v 依存性を計算し、報告されている実験値と一致を得ることができた。紫外部に観測される $X^2\Sigma_g \leftarrow B^2\Sigma_u^+$ 遷移についても同精度の計算を行ったので、計算で得た振動回転遷移確率は、定量的遠距離計測に用いることができることを示している。

　これら一連の岡田君の研究は、大気化学的に重要な 2 原子分子の分光学的諸量を精度高く計算するとともにその手続きを確立したものとして高く評価される。これらの結果は国際誌に一報が印刷済み、もう一報が印刷中であり、提出された博士論文は博士(理学)に値する内容を持つと、審査委員全員は判断し、合格と判定した。

　岡田一俊君の博士論文に関する口述試験は 2000 年 1 月 27 日午後に 2 時間半にわたって実施された。発表と質疑の中で、研究対象とした分子系に対する理解をもっていることお

および理論的方法の基礎を把握していることを示した。また、博士論文は英語によって書かれており、各章は国際的論文に投稿済みあるいは投稿できる形にまで完成されており、英語による研究成果の発表能力が十分な水準に達していると判断された。公開発表においても適切に質疑に対応することができた。

　以上により、口述試験、公開発表会の最終試験を合格したものと審査委員全員で判断した。