

$\pm 0.002$  agrees with  $0.102 \pm 0.003$ , the average of the isotopic abundance data for Ti of A. O. Nier and J. E. Hogg, as given in Lederer, Hollander, and Perlman.<sup>3</sup>

The  $\text{TiO}^+/\text{TiO}_2^+$  intensity ratios, their trends with time, and the  $\text{TiO}_2^+$  fragmentation of less than  $2.5 \pm 1.3$  percent are all consistent with the known vaporization behavior of the Ti-O system. That the value is a clear upper limit arises because the measurements were performed after some slight decomposition of  $\text{TiO}_2(\text{s})$  had occurred and because the  $\text{TiO}_2^+$  measurement was made later than the  $\text{TiO}^+$  one.

Hampson and Gilles<sup>1,2</sup> observed mass spectrometrically a  $\text{TiO}^+/\text{TiO}_2^+$  ratio of about 0.25 at the beginning of their experiments with  $\text{Ti}_4\text{O}_7$ . Even if the fragmentation of  $\text{TiO}_2^+$  is 4 percent, which is the upper limit including the uncertainty, they made a negligible error by assuming that the only source of  $\text{TiO}^+$  was  $\text{TiO}(\text{g})$ . Similarly, the work of Wu and Wahlbeck,<sup>4</sup> Liu and Wahlbeck,<sup>5</sup> Drowart, Coppens, and Smoes,<sup>6</sup> and Balducci, DeMaria, Guido, and Piacente<sup>7</sup> should not suffer because of fragmentation of  $\text{TiO}_2^+$ . Only in much more oxygen-rich phases could fragmentation of  $\text{TiO}_2^+$  cause a significant error.

The advantage of using the entire shutter profile areas instead of merely measuring intensities with shutter open and closed is that the extreme care in setting the open position, a matter of great importance for ions of low intensity, is not required. In addition, we doubt

that results with the reliability reported here could have been obtained without the data acquisition and equipment control system. So much slow human activity would have been required that the chemical system would have changed too much during the time consumed.

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## Laser isotope separation using an intracavity absorption technique\*

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Three prerequisites for the separation of isotopes by photochemical means are: (1) selective excitation of the desired isotopic species; (2) preferential reaction of the excited isotopic species with a scavenger; and (3) separation of the photoproducts from the reaction mixture without the occurrence of appreciable isotopic scrambling. In a previous report<sup>1</sup> we described the photochemical separation of  $^{35}\text{Cl}$  and  $^{37}\text{Cl}$  in which a 1:1 mixture of iodine monochloride and the scavenger, 1,2-dibromoethylene (*cis*, *trans* mixture) at 20 torr total pressure is irradiated by a cw dye laser. The dye laser has an output 3 Å wide and is tuned to the (18,0) bandhead (6054 Å) of the  $\text{I}^{37}\text{Cl} A^3\Pi_1-X^1\Sigma_0^+$  band system. The reaction products are separated by liquid-gas chromatography and analyzed using a Nier-type mass spectrometer. The photoproducts are found to be enriched in  $^{37}\text{Cl}$ . In particular, the photoproduct, *trans*-ClHC=CHCl, showed a change in the ratio of the 35 to 37 mass peak from 3.01 for naturally occurring *trans*-dichloroethylene to 2.0 for the photoproduct. It

was suggested that this isotopic enrichment could be improved if the 3 Å laser linewidth were narrowed sufficiently to pump individual  $\text{I}^{37}\text{Cl}$  absorption lines. This has been demonstrated in our laboratory using the novel means of nonlinear intracavity absorption to achieve an enrichment factor of about 17 on milligram samples.

The technique generally used for narrowing the output of a dye laser is to operate it on a single mode and to lock it to a particular absorption line (here a line of  $\text{I}^{37}\text{Cl}$ ) by means of etalons. An alternative procedure, described below, is to insert an absorption cell of  $\text{I}^{35}\text{Cl}$  inside the cavity of a broad-band dye laser, thereby locking it off those unwanted output frequencies that can excite  $\text{I}^{35}\text{Cl}$  in the external reaction mixture. The former procedure requires a detailed knowledge of the high resolution spectrum of the molecule being excited, and has the disadvantages that the dye laser delivers less power than when it is run broad band and the number  $\text{I}^{37}\text{Cl}$  molecules in the reaction mixture that can absorb the laser



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## COMMENTS

### Comment on "Semiclassical treatment of vibrational-translational energy transfer in the near-adiabatic approximation"

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Recently one of us<sup>1</sup> used a near-adiabatic (perturbed stationary states) approximation in an investigation of the collinear vibrational excitation of a harmonic oscillator. This approximation reduced the problem to that of obtaining transition probabilities for a harmonic oscillator with a time-dependent forcing function. Cady derived an apparently exact solution for this problem. We show here that this solution is not exact but that the solution results from making a further adiabatic approximation and give a derivation that clearly shows the adiabatic character of this further approximation.

The additional approximation in the earlier derivation arises from the assumption [equation below (11) in Ref. 1] that  $[H^0(t_1), H^0(t_2)] = 0$ , where

$$H^0(t) = p^2/2 + 1/2 \omega^2(t)q^2 \quad (1)$$

Here  $p, q$  are momenta and position coordinates of an oscillator with unit mass and time-varying frequency  $\omega^2(t)$ . In fact

$$[H^0(t_1), H^0(t_2)] = 1/4 \{ \omega^2(t_2) - \omega^2(t_1) \} [p^2, q^2] \neq 0 \quad .$$

Thus, the Magnus expansion was actually truncated after the first term. Popov and Perelomov<sup>2</sup> have investigated the forced oscillator with varying frequency and obtained the general solution for the wavefunction. However, because of algebraic difficulties, they were able to obtain a closed form expression only for  $0 \rightarrow n$  transition probabilities. The wavefunction has also been obtained independently by Chapuisat and Manz.<sup>3</sup>

Since we wish to use the exact solution,<sup>2</sup> we switch to their notation ( $\hbar = 1$ ) to solve the time-dependent Schrödinger equation with Hamiltonian

$$H = H^0 + f(t)q \quad (2)$$

This  $f$  is related to that used in Eq. (8) of Ref. 1, which we shall term  $f_c$ , by

$$f(t) = \sqrt{2\omega(t)} f_c(t) \quad . \quad (3)$$

The exact solution  $\psi(q, t)$  may be determined<sup>2</sup> once the solution is known of the classical equation of motion

$$\ddot{\xi} + \omega^2(t)\xi = 0 \quad (4)$$

with

$$\xi(t) \rightarrow \exp(i\omega t) \text{ as } t \rightarrow -\infty \quad ,$$

where

$$\omega(t) \rightarrow \omega \text{ as } |t| \rightarrow \infty \quad .$$

Interpreting  $\xi$  as the solution of a one-dimensional Schrödinger equation<sup>4</sup> means that we are studying reflection and transmission above the barrier  $\omega^2$ . For general functions  $\omega, \xi$  cannot be obtained in terms of standard functions. Since  $\omega$  is slowly varying in most calculations of vibrational excitation<sup>1</sup> we may use a simple WKB approximation

$$\xi(t) = [\omega/\omega(t)]^{1/2} \exp[i(\omega t + \int_{-\infty}^t \Delta\omega(t') dt')] \quad , \quad (5)$$

where

$$\Delta\omega(t) = \omega(t) - \omega \quad .$$

This form of WKB solution will be valid provided  $\omega^2 \neq 0$ , i. e., the oscillator is always subjected to a restoring force. In this approximation there is *no reflection* so that the parameters<sup>2</sup>  $\rho, \tau$ , and  $a_2$  have the values 0, 1, and 0, respectively. It is this absence of reflection which yields sufficient simplification to enable all the transition probabilities to be calculated in closed form. Using (5) the wavefunction is given by<sup>2</sup>

$$\psi(q, t) = \phi_i(q - \eta, \tau) \exp\{i[\dot{\eta}(q - \eta) + \sigma]\} \quad . \quad (6)$$

Here  $\phi_i$  is the solution of a simple harmonic oscillator of frequency  $\omega$ ;  $\tau$  and  $\sigma$  are functions only of time and  $\eta$  is the displacement of the classical forced oscillator